

NIST Analytical Chemistry Division (839)

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FY99 Division Overview and Selected Technical Reports

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The Analytical Chemistry Division (ACD) serves as the Nation's reference laboratory for chemical measurements and standards to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and provide quality assurance for chemical measurements used for assessing and improving public health, safety, and the environment. The Division's activities primarily contribute to the accomplishment of CSTL's measurement science and measurement standards goals through the efforts of its five Groups:

- Spectrochemical Methods,
- Organic Analytical Methods,
- Gas Metrology and Classical Methods,
- Molecular Spectrometry and Microfluidic Methods, and
- Nuclear Analytical Methods.

The skills and knowledge derived from laboratory-based research concerning the phenomena that underpin the measurement of chemical species in a broad spectrum of matrices are applied to the development and critical evaluation of measurement methods of known accuracy, sensitivity, and uncertainty. This expertise in chemical measurement science is deployed in a highly leveraged manner and serves as the foundation for cross-cutting chemical measurement and standards programs in:

- Advanced Materials Characterization
- Analytical Instrument Performance and Calibration
- Environmental Monitoring and Technology
- Forensics
- Healthcare
- Food

Our vision is to maximize this leverage by establishing and maintaining the chemical measurement infrastructure that provides national traceability and is the basis for assessing and improving international comparability, for chemical measurements in these and future high priority

program areas. To realize this vision we use and develop infrastructural tools such as:

- Standard Reference Materials
- NIST Traceable Reference Materials (NTRMs)
- Measurement quality assurance programs in critical national areas
- Comparisons of NIST chemical measurement capabilities and standards with other National Metrology Institutes.

Increased requirements for quality systems documentation for trade and effective decision-making regarding the health and safety of the U.S. population have increased the need for demonstrating "traceability-to-NIST" and establishing a more formal means for documenting measurement comparability with standards laboratories of other nations and/or regions. Standard Reference Materials (SRMs) are certified reference materials (CRMs) issued under the National Institute of Standards and Technology trademark. These are well-characterized using state-of-the-art measurement methods and/or technologies for chemical composition and/or physical properties. Traditionally, SRMs have been the primary tools that NIST provides to the user community for achieving chemical measurement



Analytical Chemistry

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- Spectrochemical Methods
- Organic Analytical Methods
- Gas Metrology & Classical Methods
- Molecular Spectroscopy & Microfluidic Methods
- Nuclear Methods

quality assurance and traceability to national standards.

Currently, NIST catalogs nearly 1300 different types of SRMs; in 1999 NIST sold over 33,000 SRM units to approximately 6,550 unique customers. Approximately 21,000 of the units sold were from the 850 different types of materials that are certified for chemical composition. Since it has the world's leading, most mature, and most comprehensive reference materials program, most of the world looks to NIST as the de facto source for high quality CRMs to support chemical measurements. NIST has met the reference materials needs of U.S. industry and commerce for nearly 100 years. While our reference materials program has focused primarily on U.S. requirements, it is clear that these materials address international measurement needs as well. As demonstration of quality and "traceability" for chemical measurements have become increasingly global issues, the need for internationally recognized and accepted CRMs has increased correspondingly. Their use is now often mandated in measurement/quality protocols for analytical testing laboratories. Coupled with the fast pace of technological change and greater measurement needs, the demand for additional quantities and additional specific varieties of reference materials has mushroomed. NIST, by itself, does not have the resources to provide SRMs (exact sample types, unique compound combinations, concentrations, etc.) to meet all these needs. Without a significant shift in paradigm, CSTL will not be able to address future needs for reference materials; neither nationally nor internationally.

The NIST Traceable Reference Materials (NTRM) program was created to partially address this problem of increasing needs for reference materials with a well-defined linkage to national standards. An NTRM is a commercially produced reference material with a well-defined traceability linkage to existing NIST standards for chemical measurements. This traceability linkage is established via criteria and protocols defined by NIST and tailored to meet the needs of the metrological community to be served. The NTRM concept was implemented initially in the gas standards area to allow NIST to respond to increasing demands for high quality reference materials needed to implement the "Emissions Trading" provisions of the Clean Air Act of 1990

(while facing the reality of constant human and financial resources at NIST). The program has been highly successful. Since its inception, 11 specialty gas companies have worked with NIST to certify over 7000 NTRM cylinders of gas mixtures that have been used to produce more than 475,000 NIST-traceable gas standards for end-users. According to Stephen Miller, Technical Director, Scott Specialty Gases, "the NTRM program has served as an excellent vehicle for production of the high quality standards - of known pedigree - required by both industry and the regulatory community in the implementation of Title IV [SO₂ emissions trading] of the 1990 Clean Air Act." The NTRM model for the commercial production of reference materials is being extended to other mature and high volume areas to both more effectively deliver the increasing number of NIST-traceable standards to end users and allow more of our internal resources to be diverted to address new and/or more difficult measurement problems. Immediate plans are to provide NTRMs for optical filter standards, (Spring 2000) elemental solution standards (Summer 2001), and metal alloy standards (Fall 2001). The term NTRM has been trademarked and we are in the process of obtaining a service mark to facilitate its appropriate use by commercial standards producers.

We recognize that the NTRM model is only applicable in selected areas. In the remaining areas, such as complex matrix standards, we have begun leveraging our resources through increased strategic collaborations with other National Metrology Institutes and selected U.S. laboratories. Additional details concerning our collaborative activities with both private sector U.S. laboratories and commercial reference material and proficiency testing service providers as well as other National Metrology Institutes worldwide are provided in Technical Activity Reports 12 – 18.

International agreements and decisions concerning trade and our social well-being are increasingly calling upon mutual recognition of measurements and tests between nations. The absence of such mutual recognition is considered to be a technical barrier to trade, environmental and health-related decision making. In recent years, mutual recognition agreements have been established related to testing and calibration services and in respect of the bodies accrediting such activities. All of these rest upon the assumption of equivalence of

national measurement standards and reliability of the link between national measurement standards and the relevant testing services in each country. In October, 1999, the Directors of National Metrology Institutes for the thirty-eight member states of the Meter Convention signed “the mutual recognition arrangement on national measurement standards and calibration and measurement certificates issued by national metrology institutes (MRA). This MRA had been in the works for sometimes and with this knowledge, we began taking a leading role in the activities of the International Committee of Weights and Measures-Consultative Committee on the Quantity of Material (CCQM) and Interamerican System for Metrology (SIM) – Chemical metrology Working Group. The CCQM activities are focussed on assessing, improving and documenting the equivalence of the chemical measurement capabilities among National Metrology Institutes worldwide. Our activities within SIM are focussed primarily on assessing chemical measurement needs and capabilities among the 34 member economies. We are working with CITAC (Cooperation in International Traceability in Analytical Chemistry) to harmonize the vertical traceability links in the various countries and regions around the world. Additional details concerning these activities can be found in Technical Activity report 18.

In addition to these global and regional activities we are establishing a limited number of strategic bilateral programs. For example, our collaboration with the Netherlands Measurement Institute (NMI) for determining the equivalence of primary gas standards has resulted in a formal “Declaration of Equivalence” that is recognized by the U.S. EPA and European environmental regulatory bodies as documenting the equivalence between seven NIST and NMI primary gas mixtures suites. Details concerning this activity can be found later in the Gas Metrology and Classical Methods section of this overview and in Technical Activity Report 18. We have a formal agreement with NRC-Canada (via the NAFTA Treaty) for cooperation in the development of marine environmental standards and have recently signed a Cooperative Arrangement with NIMC (Japan) for collaborative efforts in the area of pure volatile organic compound standards. Several additional strategic bilateral arrangements with other National Metrology Institutes /Standards laboratories are being discussed.

In addition to our standards activities (SRM, NTRM and strategic international comparisons), providing chemical measurement quality assurance services in support of other Federal and State government agency programs continues to be an important part of our measurement service delivery portfolio. During the past year, we were involved in 13 projects with 6 federal and state government agencies primarily providing them with measurement quality assurance services for environmental and health-related activities. Details concerning many of these have been provided in past Division overviews. Additional information concerning a relatively new activity--QA Support for Private Sector Provision of Proficiency Testing for EPA/States Drinking and Waste Water programs is mentioned later in two of the Group Sections and Technical Activity Report 17.

Brief overviews of each of the five Technical Groups within the Division follow along with 18 selected Technical Activity Reports. These overviews and reports demonstrate the diversity and breadth of our research program and the services that we provide. They also illustrate the critical synergistic relationships that exist among our research programs and activities in chemical measurement science and the standards and quality assurance services that we provide.

Spectrochemical Methods Group

Research activities in spectrochemical methods are directed toward the development, critical evaluation, and application of techniques for the identification and measurement of inorganic species using x-ray, optical, and mass spectrometries. The focus of this research is measurement accuracy and precision, benchmarking industry's needs for traceability, advanced materials characterization, and commodity value assignment and specification.

The major event of the year was the move to the Advanced Chemical Sciences Laboratory. The move of the Group to the 3rd floor of the ACSL results in a consolidation of offices and laboratories from the 1st, 2nd, and 3rd floors of the old Chemistry Building, and the basement of the Physics Building. This consolidation should allow more cohesive and coordinated work by the group, in addition to providing better functionality—sample handling laboratories and instrument laboratories are now contiguous. The move also forced an assessment of the future directions for the Group and a

consolidation of instrumentation. Thermal ionization mass spectrometers (TIMS) were loaned to the Physics Laboratory, several university laboratories, DoE, and the Institute for Reference Materials and Measurement (IRMM) in Belgium. The move punctuated the evolution away from solid source mass spectrometry to inductively coupled plasma mass spectrometry (ICP-MS) for the Group. We now have five ICP-MS; and, only two of the NBS-style TIMS instruments remain.

The X-Ray Fluorescence (XRF) team had a number of accomplishments to its credit this year, in both the measurement and research areas. A collaborative effort with a guest researcher from the Naval Research Laboratory to study and compile XRF fundamental parameters is reported as a technical highlight elsewhere in this volume. Progress continued on a collaborative project with a second guest researcher from Poland studying microbeam XRF. A significant amount of SRM work was also completed. Homogeneity testing was done for about a dozen materials in preparation. The Pb paint films of SRMs 1570–1576 were recertified with XRF played a major role in this certification effort. Three cement SRMs were certified—starting a major recertification program for these important and popular SRM materials. The cement SRM category was the only SRM category that showed increased sales for this year. SRM 1848, Lubricant Additive Package, is a new SRM under development. This SRM is top priority of the lubricants industry and is needed to satisfy their requirements for linking measurements made on finished products to recognized national or international standards. Activities leading to the development of SRM 1848 are described in more detail in Technical Activity Report 11.

The high performance ICP-OES research and measurement effort continues to impact a wide range of activities in the Group. It is an established part of the Spectrometric Solution SRM program, discussed below. In addition, we have continued to promote its broader dissemination. The previous lithium aluminate work was documented for DoE and a publication is in review. The method is now being successfully applied by DoE to qualify material to the narrow specifications allowed for producing tritium safely in a civilian reactor. The ability to achieve high performance using two other manufacturers' ICP-OES instruments was also demonstrated this year. One of these instruments

was in the laboratory of a provider of secondary standards. The experiments were done as part of a beta test of our proposed NTRM program for solution standards. The results of this collaborative work was presented at two conferences. In the international arena, we have collaborated with EMPA in Switzerland to characterize a series of elemental solutions that will be distributed as part of a CCQM key comparison (CCQM K-8). The relative standard errors of replication for the four elemental solutions prepared (Fe, Cu, Al, and Mg) were all better than 0.01 %.

The improved ICP-OES method has been presented in the context of “replacing classical analysis.” It matches the precision and approaches the understanding of sources of error of classical analysis, especially for cases where the sample can be reduced to a simple dilute solution, as is done for the spectrometric solution SRMs. We have extended the concept this year by assaying the major elements in a more complicated sample, SRMs 1775/2175, a high temperature alloy with Ni, Mo, Cr, and Co as its major constituents. A multielement experimental plan and calibration strategy was applied to determine these elements. The relative standard uncertainties for replication were 0.02 %. Because of the rigor and labor intensity required, classical analysis is an expensive and disappearing capability in analytical chemistry. The results of this work were presented to a group of analysts in the metals industry in July. These analysts echoed a common theme whenever this work is presented—“how do I procure this capability for my laboratory?” We will continue to promote the process of technology transfer both by working with manufacturers and by demonstrating and publicizing the possibilities.

One of the research areas generally studied by the Group was the improvement of instrumental performance in the presence of drift as described in one of the technical highlights. One application was in glow discharge optical emission spectrometry (GD-OES). This work identified a source of drift in GD-OES and showed how it could be accounted for by applying an appropriate calibration strategy. Subsequently, the manufacturer has made hardware modifications that should alleviate the source of the drift—an example of how our research can have immediate impact. A second research activity in GD-OES was the study of the analytical benefits of alternative and mixed gases. This work was started

through a collaboration with Clemson University and funding by NSF. Various figures of merit were assessed for glow discharges using pure Ne, Ar/Ne and Ar/He mixtures, and compared to Ar. Initial results indicate that there are only minor benefits for the extra effort expended, and this conclusion runs counter to published observations in this field. Finally, a major research effort was undertaken in the analysis of SRM 1775/2175, a high temperature alloy, this year, as part of the Division's exploration of new methods for certification of metals. The comparative results versus XRF and other methods, e.g. HP-ICP-OES described above, were instructive and showed that there is still a great deal to be learned about the technique.

Inductively-coupled plasma mass spectrometry is now the measurement workhorse for the group, continuing the trend begun in 1985 when the first instrument was procured. This year, we procured the fifth instrument for the group and installed it in the Division's laboratory in Charleston, South Carolina. The first inorganic analytical chemist to be stationed in Charleston was identified and he spent the year in Gaithersburg becoming familiar with the methods and procedures that used by the group. He moved to Charleston in August, and has overseen the completion of the inorganic facility, anchored by the ICP-MS, but also including a clean sample preparation area to allow trace element determinations. While at NIST he participated in the certification of Hg in several materials, and performed other Isotope Dilution-ICP-MS measurements. He also collaborated in a research project that investigated the coupling of a commercial cold vapor atomic absorption spectroscopy (CV-AAS) instrument with ICP-MS for mercury measurement. This method was used in the certification program for SRM 1641d Trace Mercury in Water and SRM 966 Heavy Metals in Blood. The key innovation was the ability to quantify the results using two distinct methods, including isotope dilution mass spectrometry.

Thermal ionization mass spectrometry is still the method of choice for high precision isotope ratio measurements and the Group has developed an isotope dilution mass spectrometry method for chlorine that addresses the need to quantify this gaseous non-metal in complex matrices. This work builds on a previously developed ID-TIMS method for chlorine in blood/serum that is not generally applicable to other materials; a new procedure for

high precision chlorine isotope ratio measurement; and, a new chlorine extraction procedure. This work is an extension of a postdoctoral research project to measure and understand natural variability of chlorine isotopic abundances in geological materials. The determination of concentration by isotope dilution is a logical adjunct. The pyrohydrolysis technique for extraction of the chlorine is also being investigated for extraction of mercury, and direct coupling to an ICP-MS. European and US environmental agencies recently have expressed concern about chlorine and mercury emissions in the burning of fossil fuels and proposed rules to monitor these emissions. These rules will require standards to benchmark measurement of these elements in the fossil fuels—critical measurements needed to understand and assess the magnitude of the problem. The certification of both elements in existing coal SRMs will serve this benchmarking need.

The Group took over the production and certification of the Single Element Spectrometric Solution SRM program at the beginning of the year, which included transfer of two scientists from the Gas Metrology and Classical Methods Group. The process by which these SRMs are certified was completely reengineered. A system for the production of weighed aliquots of primary standard solutions was implemented. These primary materials will serve as the basis for a new class of elemental solution SRMs designed for use as traceability transfer standards, and will be used in the development of an elemental solution NTRM program, described further in the NTRM Technical Activity Report 16.

Organic Analytical Methods

Research activities in organic analytical methods are directed toward the development, critical evaluation, and application of methods for the identification and measurement of organic and organometal species using organic mass spectrometry and analytical separations techniques. These separation techniques include gas chromatography (GC), liquid chromatography (LC), supercritical fluid chromatography (SFC) and extraction (SFE), capillary electrophoresis (CE), and capillary electrochromatography (CEC).

Recent research activities in organic mass spectrometry have focused on the development of techniques for characterization and quantitative

determination of proteins in biological matrices. We are developing a number of primary and reference methods for important biomarkers such as troponin-I (a new marker of myocardial infarction), glycated hemoglobin (an important new marker for diabetes), and serum thyroxine (an important marker for thyroid function). Techniques have been developed for the chemical characterization of purified troponin-I preparations, thus providing a means for comparing the molecular structure with results from field studies involving immunoassays. Two new LC/MS instruments are providing new capabilities for the determination of analytes of health, nutritional, forensic, and environmental importance, as well as for structural studies of natural products. Our new high-resolution mass spectrometer is being used in the development of methods for complex environmental contaminant mixtures such as dioxins, furans, and toxaphene as a prelude to future certification measurements of these substances in natural matrix SRMs. Ion-trap mass spectrometry is being combined with chemical ionization (CI) to improve the measurement of polyunsaturated fatty acids. Fatty acids such as these are found in fish oils and are believed to provide health benefits; however, their determination by mass spectrometry is hindered by their extensive fragmentation under electron ionization conditions, but with CI and acetonitrile as the source of reagent ions, it is possible to obtain strong signals for characteristic ions from these compounds. Mass calibration of mass spectrometers used for high molecular weight species is difficult and few appropriate materials are available. Research is underway to develop a set of proteins produced by bacteria grown in a media depleted in ^{13}C and ^{18}O . Such proteins will have much simpler isotope clusters which will be useful for mass calibration in matrix assisted laser desorption ionization (MALDI) and electrospray mass spectrometry of biomolecules.

Research activities in separation science continue focus on investigations of the physical and chemical processes that influence retention in LC, GC, SFC, CE, and CEC. Results from these fundamental studies are used to design stationary phases tailored to solve specific separation and analysis problems, and to assist in method development and optimization. Recently we have explored a novel approach to the synthesis of LC stationary phases based on polymer immobilization. Polyethylene acrylic acid copolymers were immobilized on silica

as an alternative to conventional silane surface modification chemistry. The resulting columns were evaluated for the LC separation of carotenoid isomers, and preliminary results indicate exceptional selectivity for this class of compounds. Further optimization of this promising stationary phase should result in improved measurement capability for carotenoids and related nutrients in food and tissue samples. Research in chiral separations is continuing in several areas using LC, CE, and GC. The determination of chiral drug species in hair samples using LC may permit environmental exposure to be distinguished from illicit use. Studies have been carried out with a model chiral compound (metoprolol) to evaluate the potential of this approach, for eventual application to amphetamine and methamphetamine. In other studies, functionalized cyclodextrins have been evaluated as chiral selectors in CE. The use of dimethyl-, hydroxypropyl-, and sulfated- forms of β -cyclodextrin improve aqueous solubility and alter the chiral recognition properties of this compound. Finally, chiral GC methods have been developed for the determination of DDT and DDE in environmental samples where enantiomeric resolution required coupling of chiral and achiral columns.

Insights gained from our research in separation mechanisms have provided us the knowledge to develop two new LC column performance test mixture SRMs. SRM 870, Column Performance Test Mixture, will be used to characterize LC column properties such as silica silanol activity, trace metal activity, and separation efficiency. SRM 877, Column Selectivity Test Mixture for Chiral Separations, will be useful in predicting the performance of columns for resolving enantiomers.

Our research in organometal speciation has continued with improvements in the GC-atomic emission-based method for methylmercury and alkyl tin species. The new approach involves derivatization and a solid phase micro-extraction (SPME) step to concentrate the analytes and has been used to provide data for certification of methylmercury in SRM 2977 Mussel Tissue and SRM 1566b Oyster Tissue. During the coming year the method for methylmercury will be applied to additional SRMs including SRM 1946, Lake Superior Fish Tissue, and SRM 966, Toxic Metals in Blood. This same general approach will also be used to measure tributyltin in several of the marine

matrix SRMs. Other research has involved development of multidimensional chromatographic approaches for quantification of non-ortho polychlorinated biphenyl congeners (considered to be the most toxic congeners) in some of our existing cod liver oil, sediment, and whale blubber SRMs, and nitro-substituted polycyclic aromatic hydrocarbons in diesel-related SRMs.

We have developed a method using pressurized fluid extraction and GC/MS or GC with electron capture detection to assess the micro-homogeneity of organic contaminants in natural environmental matrices. The method has been applied to air particulate, diesel particulate, frozen mussel tissue, and sediment SRMs. For the air particulate SRM, the amount of material that yields a 1% sampling error (due to heterogeneity) varies with analyte from approximately 50 mg to 450 mg, whereas the amount of diesel particulate material that yields a 1% sampling error varies only between 40 mg and 80 mg. Certificates of Analysis for these SRMs will be updated with this new information.

Even with the downtime experienced by the move to our new quarters, a number of high priority natural matrix SRMs were completed this past year. These were:

- **SRM 1546 Meat Homogenate**, which was identified by the USDA, FDA, and the food industry as a high priority need was completed with certified values for cholesterol, six fatty acids, calcium, sodium, iron, and total nitrogen, and reference values for proximates, calories, a number of other fatty acids, and some additional nutrients.
- **SRM 1944, New York/New Jersey Waterway Sediment**, with over certified values for 70 species including several polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, and trace elements. Reference Values were provided for 80 additional species including selected polychlorinated dibenzo-p-dioxins(PCDDs) and dibenzofurans(PCDFs)
- **SRM 1649a, Urban Air Particulate Matter**, has certified/reference values for over 100 PAHs, PCBs, chlorinated pesticides, and PCDDs/PCDFs, as well as values for total organic carbon, percent extractable material, carbon composition, particle-size information, and trace elements.

- **SRM 1589a, PCBs in Serum**, has PCBs at naturally occurring levels in contrast to its predecessor where high levels of Aroclor mixtures were spiked into serum. This replacement material has been analyzed at NIST and the Center for Disease Control to provide certified and reference values for PCBs, chlorinated pesticides, and PCDDs/PCDFs.

A number of new SRMs are nearing completion. Details concerning these activities can be found Technical Activity Reports 12-14.

The research and standards development activities within this Group have resulted in over 50 manuscripts either submitted, in press, or published in refereed journals during the past year. Nine papers were published or accepted by the journal *Analytical Chemistry*, two of which were featured in the "A" pages, which are authoritative, high visibility reviews of specific topics written for a broad audience.

Gas Metrology and Classical Methods

Research activities within the Gas Metrology and Classical Methods Group are focused on gas metrology, classical wet chemical methods (gravimetry, titrimetry), coulometry, ion chromatography, and maintenance of the theoretical infrastructure for pH and conductivity measurements.

This year the move into the new building interrupted our programs for approximately three months. Despite this, we have had a very productive year due to the dedication and hard work of our staff. As seen below, this interruption had little effect on the number of SRMs, NTRMs, and Data Products delivered by this group. Also despite the move, the group was able to provide two courses, one of Classical Methods and the other on Gas Metrology, for representatives from other national standards laboratories within the Americas. These courses were very well received and are the only ones scheduled for repeat during the coming year.

During FY99 the following SRMs were completed; 15 gas cylinder, 3 anion solution, 12 conductivity, 2 ion activity, 6 Volatile Organic Compound solutions and a zeolite material. A total of 170 gas cylinder SRMs were recertified for 15 companies. While these certified reference materials are

critically needed, their continuous production consumes considerable fiscal and human resources and limits our ability to address new standards needs. The gas NIST Traceable Reference Materials (NTRM) Program was created to address this concern. In FY99, we worked with 7 specialty gas vendors to certify 66 NTRM batches. The over 1000 individual gas cylinders in these certified batches will be used to produce approximately 100,000 NIST-traceable gas standards for end-users. Over the next year we will be defining a new approach for gas NTRM certification which will allow Specialty Gas Companies to expand their production while still maintaining the strong linkage to National Standards maintained at NIST.

Over the past year we have restocked all conductivity solution SRMs, thus recovering from a shutdown of this program two years ago when the person responsible for this program left NIST. In the past, leakage and transpiration limited our certification period to less than 1 year. Based on a pilot study involving three of our prime customers, we determined that switching to serum bottles provides stability for more than two years. We are planning on moving all conductivity solution SRMs into this bottling scheme in the next year. In addition we have revived an intercomparison with Hungary and Denmark on conductivity, and have championed a paper on molality-based electrolytic conductivity through IUPAC.

The area of pH standards continues to receive much international attention. Our active participation in IUPAC Commission V.5 resulted in acceptance of the Bates-Guggenheim convention, thus assuring continued traceability of pH to sound thermodynamic principals. We were also instrumental in defining the recommended values of uncertainty for the draft document on pH standards. This effort caps a three-year activity to defend the present pH scale from a simplified, yet non-traceable, scale championed by a few participants in V.5. Conversion to a new scale would have needlessly impacted U.S. industry financially. As a result of our active leadership in V.5, Ken Pratt has been nominated for Titular Membership in IUPAC. NIST also participated in both CCQM and European Union intercomparisons on pH. We have also organized an intercomparison to assess pH measurement capabilities within SIM.

Other activities in the classical methods program include research to improve the quality of our anion solution SRMs and certification of Si in a zeolite material using gravimetry coupled with XRF to account for additive interferences. This approach allowed the certification of Si in the Zeolite SRM with a relative uncertainty of 0.1 %.

In collaboration with EPA and the remote sensing community, we have developed a quantitative database of infrared spectra, which is required for establishing FTIR-based technology as a reliable tool for real-time monitoring for airborne chemical contaminants along plant boundaries and within plant facilities. Because the spectra are being prepared using NIST primary gas standards, well-defined traceability to NIST can be established for any subsequent field measurements. These spectra will be required to be used in the new update of EPA method TO-16. More information concerning this activity, and the most recent release of a CD-ROM containing spectra for 30 high priority species, can be found in Technical Activity Report 7. Future efforts will address continued data acquisition for compounds listed in the 1990 Clean Air Act amendment that are measurable with FTIR as well as additional compounds that contribute to global warming and ozone depletion.

In June 1999, the Ozone standards activities were transferred from the Surface and Microanalysis Division and integrated into the Gas Metrology program. NIST ozone standards effort supports a network of 22 Reference Photometers that provide NIST traceability for ozone measurements for the EPA and many International agencies. These Standard Reference Photometers (SRP) were designed and built at NIST and certified against the U.S. National Reference Photometer maintained at NIST. Currently we are upgrading these field photometers with new hardware and software

To assist the U.S. automobile industry, we are developing and evaluating new analytical measurement tools and providing standards needed to address compliance issues associated with the Clean Air Act of 1990. We are developing an infrared-based sensing device and are working with the NIST Physics Laboratory to evaluate a new Fourier Transform microwave device for real-time detection of oxygenated hydrocarbons in automobile exhaust. A series of new cylinder-based gas SRMs for low emission vehicles also are being

produced to support U.S. automobile manufacturers in the development of the next generation of “clean” cars. For example, we are currently developing low concentration ($<5 \mu\text{mol/mol}$) nitric oxide gas standards to meet future regulations on automobile emissions. This effort will take approximately one additional year to complete and will result in new gas cylinder SRMs, since these standards are not suitable for the NTRM program. We will be collaborating with the Netherlands Measurement Institute and the National Physical Laboratory of the UK in this effort.

Molecular Spectrometry and Microfluidic Methods Group

The Molecular Spectrometry and Microfluidic Methods Group conducts research on or has responsibility for:

- the metrology of molecular spectrometry and develops standards for calibration, validation, and performance of instruments for measuring molecular spectra;
- conducts research on microfluidic devices, methods, and applications for chemical analysis including studies of materials and material properties affecting the flow of liquids in microchannels and the use of microchannel and other electrophoretic methods for forensic and toxicological applications and standards;
- the development and certification of optical transmittance and wavelength standards in the ultraviolet, visible, and near-infrared spectral regions; and
- works with users and manufacturers of analytical instruments to assess and measure the performance of analytical methods and to determine and address existing and future needs for analytical instrument standards ranging from device calibration and instrument performance through specifications for remote device control and data interchange.

In FY99, 102 solid absorbance filter SRMs were certified, and 189 optical filter sets were recertified. In addition, 250 units of SRM 2034 (holmium oxide uv-vis wavelength standard) and 98 units of SRM 2035 (NIR transmission wavelength standard) were certified. Measurements were completed on a 100 unit batch of SRM 2035a and research was conducted on a reflectance version of this material that will be designated SRM 2036. Development was begun on SRM 2037, a standard for calibrating the amounts of the red dye used to mark off-road diesel fuels for tax purposes, by acquiring a bulk material that contains the required Solvent Red 26 dye in ~ 85% purity. After further purification, the material will be certified for molar absorbance at two wavelengths in representative solvents. The new high accuracy reference uv-vis spectrophotometer was moved and installed in the ACSL. The software to control the instrument components was completed and validation and verification of the spectrophotometer has begun. A intercomparison of uv-vis absorbance filters (both gray glass on metal-on-fused-silica filters) was

conducted between NPL, NIST-PL (vis only), and NIST-CSTL. All of the measurement results were within the uncertainty limits over the ranges that we support.

Three glasses (a chromium glass for 785 nm, a uranium glass for 532 nm, and an europium glass for 1064 nm) have been identified as promising candidate source intensity correction standards for Raman systems with 785 nm, 532 nm, or 1064 nm lasers. These glasses provide fluorescence spectra that, when calibrated against a standard white light integrating sphere source (calibrated by the NIST Optical Technology Division), can be used to correct Raman spectra for laser color and intensity variations. This in turn will allow Raman spectra to be made essentially instrument independent and will facilitate the development of Raman spectra libraries. At present, the chromium glass has been characterized sufficiently well to permit its being sent out to ASTM Raman subcommittee members for a round robin evaluation.

A program to develop standards for luminescence spectrometry was initiated with a Workshop at NIST attended by over 40 scientists including representatives from five National Metrology Institutes. Over 60 candidate substrates, glasses and fluor-impregnated PTFE materials, have been examined for their potential as fluorescence standards. In collaboration with the Biotechnology Division, we have begun developing a fluorescein solution SRM that will be certified for purity and for concentration. The material is to be used to peg the MESF (moles of equivalent soluble fluorophore) scale used in flow cytometry.

The optical filters NTRM program was announced publicly at a Pittcon Workshop in Orlando, FL and in two articles in Spectroscopy magazine. A NIST Special Publication (SP 260-140) and a supplement to NVLAP Handbook 150 that define this NTRM program were written, reviewed, and are now being sent to interested parties with an invitation to enroll in the initial class of NTRM producers. At least four companies are expected to participate and begin selling NTRM gray glass optical filters early in 2000.

We have initiated a project through the Office of Law Enforcement Standards at NIST to advance and support the concept of quantitative measurements for forensic analysis. Specifically,

we have been developing a quantitative extraction and analysis method for the recovery of gunpowder additives based on ultrasonic liquid extraction and micellar capillary electrophoresis. In FY99, the technique was used to quantitatively compare the chemical composition of gunpowder residues to unfired gunpowder for identification. We are embarking on an effort to develop a standard reference material "Additives in Smokeless Gunpowder" that will help law enforcement agencies such as ATF and FBI to validate measurement methods for the composition of gunpowder and residue samples that are submitted for forensic identification.

We have partnered with the Electronics and Electrical Engineering Laboratory on a project supported through the NIST Advanced Technology Program to design and build silicon chips with microheating elements combined with channel interconnects in silicon, to devise methods for linking silicon chips to plastic microfluid devices, and to test heater operation in fluids for coupling to chemical reactions. We developed some new concepts to fabricate devices for this project and have leveraged some of the knowledge acquired in the course of this work to design new devices for a "Microscale Analytical Laboratory" project discussed in Technical Activity Report 6.

In conjunction with the Biotechnology Division, we provided the data analysis, analysis justification, value assignment, and certificate modification required for the recertification of SRM 2390, RFLP Profiling Standard. All forensic laboratories performing RFLP measurements are now required to analyze this SRM at least once a year to be eligible to receive Federal funding. Working with Guest Researchers from the Fochhochschule in Wiesbaden, Germany, we have extended our previous efforts to develop a device capability dataset (DCD) concept to the system level, defined and documented the system capability dataset (SCD), implemented a DCD for the HP 8453 spectrophotometer, and detailed the handling of result data by the SCD. Oliver Borchert received a second prize for his poster on dealing with result data using an SCD at the LabAutomation 99 conference in San Diego.

Nuclear Analytical Methods

Research activities in this group are focused on the science that supports the identification and quantitation of chemical species by nuclear analytical techniques. Current laboratory research activities involve the full suite of nuclear analytical techniques including instrumental and radiochemical neutron activation analysis (NAA), prompt gamma activation analysis (PGAA), and neutron depth profiling (NDP), as well as applications of neutron focusing technology for analytical applications. The measurement capabilities that reside within this group provide an excellent complement to those in the Spectrochemical Methods Group in that they depend upon characteristics of the nucleus of the element rather than the electron shells, and therefore are insensitive to chemical state. In addition, the nuclear analytical are generally nondestructive and thus do not require sample dissolution.

NAA is a powerful reference technique that has been used at NIST for many years. New developments continue to provide improvements in detection sensitivities, elemental specificity, precision, and overall accuracy that allow it to address new measurement needs. We have recently been developing Instrumental NAA procedures and applying them to study the homogeneity of SRMs at small sample sizes. Many analytical techniques used in industry and academia rely on the analysis of very small samples (i.e., 1 mg), typically in the solid (undissolved) form. Unfortunately most SRMs are certified with minimum sample sizes of 100-500 mg, and are therefore unsuitable for use as control materials for these techniques unless additional information is made available. Taking advantage of the sensitivity and nondestructive properties of INAA, the use of this technique for homogeneity studies of small samples has been evaluated and implemented for the determination of sampling characteristics for a number of environmental SRMs. The minimal analytical uncertainty associated with the INAA measurements allows extraction of the variability due to material inhomogeneity from the observed total variability in a set of measurements. We have investigated three sediment materials that have shown the potential for a high degree of homogeneity at very small sample sizes for possible use as a future SRM aimed at solid-sampling analytical techniques. From the

candidate materials a portion of the Baltimore Harbor Sediment, currently under certification for organic constituents (SRM 1941b) was selected for further processing as SRM for trace elements as well as for microanalytical techniques. Evaluation of the Ingamells model describing homogeneity has been initiated with the Statistical Engineering Division.

Instrumental neutron activation analysis has been used as a primary method for certification of the arsenic implanted dose in SRM 2134, Arsenic Implant in Silicon. This material has been a high-priority need of the semiconductor industry for a number of years. It was produced and characterized in collaboration with the Surface and Microanalysis Science Division and is intended for use as a calibrant for secondary ion mass spectrometry. The INAA results used for certification contains the first complete, quantitative evaluation of all sources of uncertainty in an INAA measurement. The expanded relative uncertainty for the mean value of this SRM was 0.38 % and approximates the 95 % level of confidence.

Significant advances have been made this year in the use of state-of-the-art signal processing techniques in our gamma-ray spectrometry systems that are used for INAA. Losses through pulse processing dead time and pile-up are best assayed with an external pulse technique. In this work, the virtual pulse generator technique as implemented commercially with the Westphal loss free counting module has been set up and tested with four high resolution gamma-ray spectrometers. Dual source calibration and decaying source techniques were used in the evaluation of the accuracy of the correction technique. Results demonstrated the reliability of the LFC with a standardized conventional pulse processing system. The accurate correction during high rate counting, including during rapid decay of short-lived activities, has become the basis for highly precise determinations in reference materials studies.

Pioneering research is conducted by this Group on the use of cold neutron beams as analytical probes for both PGAA and NDP. PGAA measures the total amount of an analyte present throughout a sample by the analysis of the prompt gamma-rays emitted immediately following neutron capture. NDP on the other hand, determines the concentrations of several important elements (isotopes) as a function of depth

within the first few micrometers of the surface by energy analysis of the prompt charged particles emitted during neutron bombardment. Both of these techniques continue to make important contributions in the characterization of advanced materials, particularly with the enhanced sensitivities now available using cold neutrons from the NIST Reactor.

A method has been developed and an apparatus built to produce titanium (and other metal) SRMs of known hydrogen concentration on the few-kilogram scale. The method is based on the controlled reaction of hydrogen with titanium in a closed system. Homogeneity is checked by neutron incoherent scattering, and concentration is verified by cold-neutron prompt-gamma activation analysis and gravimetry. The first SRM material has been prepared near the critical level of 100 mg/kg. In addition, new materials will be prepared at two bracketing levels. The apparatus has also been used to prepare standards for neutron-tomographic nondestructive analysis of turbine blades at McClellan Air Force Base.

We are currently developing and critically evaluating a nondestructive technique to quantitatively determine hydrogen based upon neutron scattering. This will serve as a complement to PGAA measurements for this element. The incoherent scattering cross section of neutrons by the H nucleus is much greater than that of any other nuclei; and the H scattering cross section is much greater than the absorption cross section. These two properties accentuate the potential of neutron incoherent scattering (NIS) for rapid H determination. In addition, NIS has very-limited overlap of error sources with PGAA, and agreement of results between the two techniques provides a high degree of confidence.

We have begun measurements of nitrogen in chemical vapor deposited diamond films by NDP. Several problems have been identified including the elevated background from gamma-ray induced electrons. While the initial results are encouraging, more effort needs to be made to improve the signal-to-background levels. These improvements will be useful in future measurements of SiON, which is of importance to the next generation of semiconductors. We are continuing our measurements of lithium migration in thin films, as applied both to electrochromic multilayers and to

lithium batteries. NDP is well suited to these studies as lithium mobility can be observed in “real” time.

The cold-neutron PGAA and NDP spectrometers, which are available to outside researchers as part of the NIST Center for Neutron Research “national users’ facility”, continue to provide high-quality measurements for outside scientists. Current experiments of interest at the NDP instrument include the measurement of shallow-doped boron content in silicon in conjunction with Advanced Micro Devices, calibration of boron in-house standards for Lucent Technologies, and the characterization of boron and nitrogen thin films in a wide variety of materials for high tech applications.

Non-destructive, matrix-independent measurements of hydrogen by the cold neutron PGAA technique have become particularly valuable in view of the difficulties of accurate determination of this element by other techniques. Many of the current PGAA experiments involve measuring hydrogen in a wide variety of materials for different applications. These include: metal embrittlement studies, studies of materials for new types of lithium batteries and fuel cells, and the determination of H concentrations for materials prior to neutron scattering measurements. PGAA has also been used along with neutron incoherent scattering (NIS) to map the hydrogen content of wet concrete samples as a function of position in an effort to create a moisture profile of the material and hence monitor the uniformity of drying. Other measurements made at the PGAA facility this year include: the determination of H, S, Ca, and K in Nafions, derivatives of Teflon which have potential use as membranes in electrochemical separations and in fuel cells; the characterization of antiferromagnetic materials which are of interest to the superconductor industry; and the analysis of a Martian meteorite, to serve as a prototype spectrum in the design of a PGAA instrument for analysis of the Martian surface. PGAA has also been used with focused neutrons has been used in the determination of chromium in a chromite layer deposited on steel casings which are used in Kraft recovery boilers by the pulp and paper industries for process chemical recovery.

Efforts continue within the group to develop the techniques and methodology of focusing cold neutron beams for analytical applications of PGAA

and NDP. A monolithic lens consisting of a fused tapered bundle of polycapillaries that provides a smaller focus of about 0.15 mm (FWHM at the focal spot) has been installed in the NDP chamber. The chamber has also been modified to accept a separate lid through which the lens can be mounted for remote-controlled alignment. A new alignment system containing a CID camera with vacuum capability has also been installed. It provides a spatial resolution of 12 μm (pixel size) and an 8 bit dynamic range for the neutron intensity, and provides the possibility for charged particle imaging. Together with the new vacuum-compatible motion stages, the alignment system permits measurements without breaking the vacuum. Furthermore, the lens can be retracted out of the beam for measurements on the same sample with normal NDP geometry. The new lens and focusing system now gives us the capability of measuring samples as small as ~ 0.1 mm in diameter or, together with our current scanning system, of measuring concentrations in three dimensions with much improved spatial resolution. Previously, our three dimensional profiles were performed with beam spot sizes of 1 cm.

The Group organized and conducted the highly successful “Tenth International Conference on Modern Trends in Activation Analysis” in April 1999. This quadrennial meeting brings together the worldwide community to assess nuclear analytical techniques and their applications, with emphasis on innovative recent developments. This session was attended by 204 scientists from 37 countries.

Future Directions

All Division research and service projects are reviewed on an annual basis for quality, progress, and match to mission and customer needs. The chemical measurement science and cross-cutting program areas on which the Division’s research and measurement service activities are focused will not change very much in the coming year. We will continue to redirect some of our efforts to expand our programs in analytical instrument calibration transfer and performance and clinical biomarker standards. As mentioned earlier, we are beginning a major new effort in microanalytical device measurement technology.

We will continue to focus more of the Division's resources on chemical measurement science and the

development SRMs with improved accuracy and uncertainty levels, and expand our collaborations with commercial reference material suppliers for providing NIST- traceable secondary standards to meet day-to-day end- user needs. The Division's budget for Standard Reference Materials activities has been ~\$3M for each of the past several years. During this period, the majority of our efforts have focused on renewals urgently requested by customers and few resources have remained for development of standards to address new measurement problems/needs. The gas NTRM program described previously has provided some relief and over the past three years, we have been able to initiate efforts for development of a number of new, high priority SRMs including the following that will completed during the coming year:

- **Aircraft Alloys** (P and S to be certified; materials failure related to P and S concentration)
- **Drinking/Wastewater Standards** (to provide accuracy benchmark and measurement traceability for proficiency testing of >5000 environmental laboratories conducted by commercial providers)
- **Fish Fillet** (PCBs, pesticides, methylmercury and food proximates to be certified)
- **Isotopically-depleted Protein Mass Standards** (with 831; for use in calibrating mass scale in 1,5000-50,000 dalton range)
- **Lubricating Oil Additives** (to certify 12 elements for providing QA and required measurement traceability for \$5B/yr Lubricants Industry)
- **Moisture in Crude Oil** (moisture levels, like sulfur, greatly influence price of crude oils)
- **Transmission NIR Wavelength Standard** (For precise calibration of spectral region of increasing industrial interest)
- **Zeolite Catalysts** (Na, Si, Al, Fe, and trace metals to be certified)

In addition, work is continuing on multiyear projects with SRMs scheduled for completion in FY01 for the following:

- **Cardiac Troponin I** (new definitive biomarker of heart attack not being effectively utilized due to measurement problems)
- **NIR Transflectance** (wavelength standards suitable in form for calibration of single- and

double-pass transmission in both wavenumber and wavelength)

- **Liquid Baking Chocolate** (to complement suite of SRMs developed in response to new nutritional labeling laws)
- **Frozen Spinach** (to complement suite of SRMs developed in response to new nutritional labeling laws)
- **Antibiotics in Milk** (for QA of HPLC tests used to accept/reject >50,000 lots of milk per year)

Work will begin during the coming year on several new SRMs for new clinical diagnostic markers.:

- **Folates** (important antioxidants; neural tube defects and blood homocysteine levels)
- **Homocysteine** (marker for heart attack risk)
- **Glycated Hemoglobin** (diabetes diagnostic marker)
- **Ionized Calcium** (important marker for diagnosis of various disease states such as skeletal resorption and stone formation in the urinary tract)
- **Thyroid Stimulating Hormone** (marker of thyroid function)
- **Speciated Iron** (marker for anemia and hemochromatosis; to address clinical need to measure iron associated with various iron-containing proteins)
- **Bilirubin** (marker for liver function)
- **Total and Speciated Selenium** (to support clinical monitoring in the relatively narrow range of beneficial effect}

The major driver for this escalation of our clinical standards program is an in Vitro Diagnostic Devices Directive (IVDD) scheduled for initial implementation in December 2003. The directive requires all manufacturers of IVDD products sold in Europe to have an "EC Stamp", verifying that they comply with the conditions of the directive. U.S. companies are major exporters of IVDD products to European markets, and thus are directly affected by the directive. One of the major components of this directive is a requirement that products be traceable to "standards of the highest order", e.g., nationally/internationally recognized certified reference materials (CRMs). At present, neither CRMs nor reference methods are available for most of the "A list" analytes that are well-defined chemical species of which there are approximately

80 ,and “B list” analytes that are less well-defined and number in the hundreds.

Additional SRMs projects being initiated this year include the following :

- **Low Sulfur in Gasoline** (to support proposed US regulation of sulfur content in gasoline for EPA Tier 2 Clean Air Act Amendments)
- **Low Nitric Oxide Standards** (to support measurements needed for development of very low emission vehicles and future automobile emissions regulations)
- **Anion Solutions** {nitrate, bromate, chlorate, chlorite, and cyanide)
- **Gravimetric Elemental Primary Standards** (“Mole standards for metals”)
- **Very Volatile Organic Compounds in Methanol**
- **Organics in Household Dust** (for toxic organic contaminants such as pesticides and PAHs)
- **Fluorescein Fluorescence Intensity** (for calibration of instrumentation widely used by clinical and biotechnology communities)
- **Trans Fatty Acids in Foods** (to support proposed trans fatty acid measurements/nutritional labeling for foods)
- **Anode Tin** (to certify lead and material purity in this important steel coating material manufactured, used, and recycled worldwide; lead content of the recycled high-value tin is of particular importance for food safety, product liability, and environmental concerns)
- **Gunpowder Composition** (to validate forensic methods used to identify gunpowder residues)

Approximately 25 SRM renewals will be completed and efforts will begin for re-certification of an additional 15 or so high priority materials. For the longer term future, we plan to re-institute the NIST program in luminescence standards. The highest priority will be the development of SRMs for fluorescence measurements.

We expect that the NTRM approach will continue to expand as the basis for allowing the commercial sector to provide reference materials to end-users with a well-defined traceability linkage to NIST. Our Optical Filter Standards program will begin in January 2000 with our Elemental Standard Solutions and metal Alloys programs following about a year later. High quality SRMs will continue to be developed to address both national and international measurement problems, but they will

be much more expensive and targeted for purchase primarily by other national metrology institutes and commercial producers/distributors. Increasingly, end-user needs will be met via NIST-traceable commercially produced reference materials.

The complex nature of chemical measurements coupled with the increasingly global nature of trade, health, and environmental issues speaks to the need for having the world make measurements using a common “meter stick”. The comprehensive nature of the NIST program in chemical measurements puts us in position to make a very significant contribution to the international chemical measurements community in this regard. In order to do this in both a cost-effective and internationally congenial manner, we are investigating opportunities for partnering with other highly qualified NMIs to provide high quality Certified Reference Materials in specific standards areas. Potential advantages of these proposed partnerships include increased supply, breadth and quality of reference materials for the worldwide chemical measurements community as well as less duplication of effort for more efficient use of limited resources.

The information that has been provided represents a broad range of research and service activities within the general area of chemical measurement science. This overview plus the Selected Technical Activity Reports that follow provide additional details concerning our work and reflect the high quality of our staff. This information also shows how our efforts are impacting U.S. industry's productivity and competitiveness as well as providing measurement infrastructural support for environmental quality and human health assessments.

Selected Technical Reports

1. *Development of a Neutron Incoherent Scattering Method to Quantify Hydrogen in Metals*

H. Chen-Mayer, R. M. Lindstrom, D.F.R. Mildner, and M. Blaauw (Interfaculty Research Institute, Delft, The Netherlands)

Objective: To develop and critically evaluate Neutron Incoherent Scattering for the determination of hydrogen in metals.

Problem: It is well known that hydrogen causes embrittlement in metals. Methods used in industry for determining H in metals are highly matrix dependent. Therefore, the metals industry requires SRMs containing H in a variety of alloys to calibrate and verify laboratory methods. Although we have one method based on PGAA for non-destructive H determination, a second method is highly desirable for confirming analytical results. The new measurement method is based on the incoherent scattering of neutrons by the H nucleus, which differs from PGAA in that the latter relies on the absorption of a neutron and subsequent emission of a 2.2 MeV gamma ray by H.

Approach: The incoherent scattering cross section of neutrons by the H nucleus is much greater than both the scattering cross section of any other nucleus and the absorption cross section of H. These two properties of the neutron interaction with H establish the potential of using neutron incoherent scattering (NIS) for H determination with higher efficiency and better sensitivity than PGAA. Since measurements can be made in minutes, compared to hours for PGAA, the NIS technique can be used effectively to study homogeneity. PGAA, however, is much more selective and matrix independent. The two techniques have a very limited overlap of error sources, and therefore, agreement of results between the two techniques provides a high degree of confidence.

A good understanding of the neutron scattering mechanism is needed for each type of sample analyzed by NIS. The value of the scattering cross section depends on the binding state of H, i.e., whether it behaves more like a free gas (scattering is in the forward direction), or is rigidly bound to the matrix (scattering is isotropic). We have built a test system to measure scattering in both forward and backward directions to determine which of these mechanisms is appropriate. Using standard addition techniques and making the assumption that H is rigidly bound in metals, we have obtained quantitative results that are in agreement with PGAA measurements.

Results and Future Plans: We have determined H concentrations by NIS measurements in a series of titanium alloys (45-350 $\mu\text{g-H/g-Ti}$), and compared the results with those obtained by PGAA. All values are in agreement with the exception of one sample at 300 $\mu\text{g/g}$. Further investigation is required to understand this discrepancy. We have studied H loading dynamics in a rare-earth window coating material used for reversible opacity control. The window opacity is altered by varying the hydrogen gas pressure which in turn affects the subsequent hydride formation within the material. When conditions are varying, a fast probe like NIS is indispensable. PGAA is not an appropriate technique for these measurements since it can only provide quantitative information when the system is in a steady state. We are currently testing a series of samples containing approximately 100 $\mu\text{g-H/g-Ti}$ to be used as a future SRM. The NIS method's advantage of rapid determination allows scanning measurements of large metal sheets to obtain information on concentration uniformity. Currently, the experimental station is time-shared with other measurement applications, and each time the equipment is changed a complete background reduction effort and a new calibration is required. We intend to build a permanent chamber with neutron-black walls and a high precision sample-positioning device for the NIS measurement, with which the critical evaluation of the technique can be completed.

2. Synthesis and Characterization of Novel Stationary Phases for Liquid Chromatography

L.C. Sander, M. Pursch, and J. Wegman (Univ. of Tuebingen, Tuebingen, Germany)

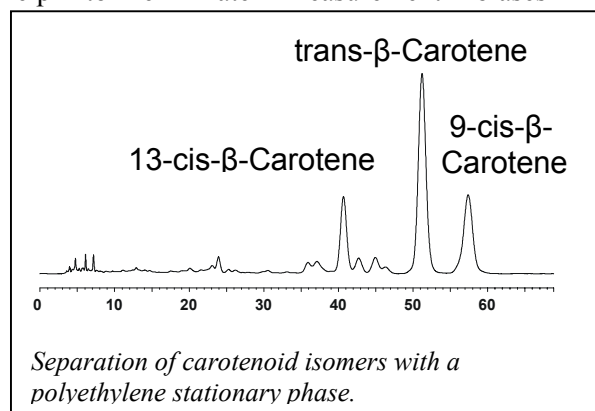
Objective: To enhance NIST capabilities for determination of isomeric species in natural-matrix samples through development of novel chromatographic stationary phases.

Problem: The liquid chromatographic (LC) separation of certain classes of isomers can present a significant challenge to the analyst. In addition to polycyclic aromatic hydrocarbons (PAHs), carotenoids and certain other nutrients are examples of compounds that occur in highly isomeric mixtures. The complexity of these mixtures is increased by other sample matrix elements, adding to the difficulty of analyses. Because the biological activity of contaminants and nutrients differ with molecular structure, measurement of individual isomers is required for assessment of potential adverse or beneficial health effects. Conventional commercial C₁₈ columns do not exhibit sufficient inherent selectivity toward shape-constrained isomers to permit determination of many such species.

Approach: In recent years, research efforts within the Organic Analytical Methods Group have been directed toward improving analytical measurement capability for carotenoids, retinoids, tocopherols, and related nutrients in foods and blood serum. Part of this effort has involved the synthesis and characterization of novel LC stationary phases with enhanced selectivity toward carotenoid isomers. A highly successful result of this research has been the development of a column based on a polymeric C₃₀ surface modification scheme. Further improvements in column performance are anticipated by the development of stationary phases based on longer alkyl chain lengths. Unfortunately, suitable reagents to prepare such long chain length stationary phases are not commercially available and cannot be synthesized in practical quantities or sufficient purity. To overcome these difficulties we have utilized a novel approach to surface modification involving immobilization of a poly(ethylene-co-acrylic acid) polymer by chemical and physical means.

Results and Future Plans: A series of stationary phases were prepared with poly(ethylene-co-acrylic acid) polymers with different composition. Three approaches to immobilization were studied: aminopropyl linkages, glycidoxypentyl linkages, and physical immobilization (i.e., no chemical bond). Columns were prepared and characterized by use of SRM 869 "Column Selectivity Test Mixture," candidate SRM 870 "Column Performance Test Mixture," and various carotenoid isomer mixtures. Initial results are extremely encouraging. Columns exhibited high chromatographic efficiency with symmetric peak shape, and retention behavior was highly shape-selective. Most importantly, separation of several important carotenoid isomers was achieved with the new polyethylene columns (Cf. figure).

The results shown represent our first efforts using this new synthetic approach. Optimization of column performance will require further study of the reaction parameters, including polyethylene copolymer composition, reagent concentration, type of covalent linkage, choice of silica, and reaction time. It is anticipated that the improved selectivity exhibited by polyethylene stationary phases will help to eliminate measurement biases for



carotenoids that result from component coelution.

3. Maximum Likelihood Cosine Inversion for Dynamic Range Extension of Interferometric Spectra

M.L. Salit and J.C. Travis

Objective: To demonstrate the utility of optical interferometry in the UV and visible spectral regions for precise and accurate optical isotope ratio determinations; and to characterize “Maximum Likelihood Inversion” as an approach for obtaining spectra with physically meaningful noise distributions.

Problem: Fourier transform spectrometry has dominated grating spectrometry in the infrared spectral region for some years, due to the so-called multiplex advantage associated with acquiring data simultaneously at all available wavelengths. Technical advances in computing technology, control systems, and optical component fabrication over the past decade have made possible the successful operation of Michelson interferometers at shorter wavelengths – extending well into the UV – but without the multiplex advantage shown in the IR. Indeed, FT/UV is widely characterized as having a “multiplex disadvantage” resulting from the artificial redistribution of noise in the spectrum by the mathematical Fourier transform used to derive a spectrum from a Michelson-measured interferogram.

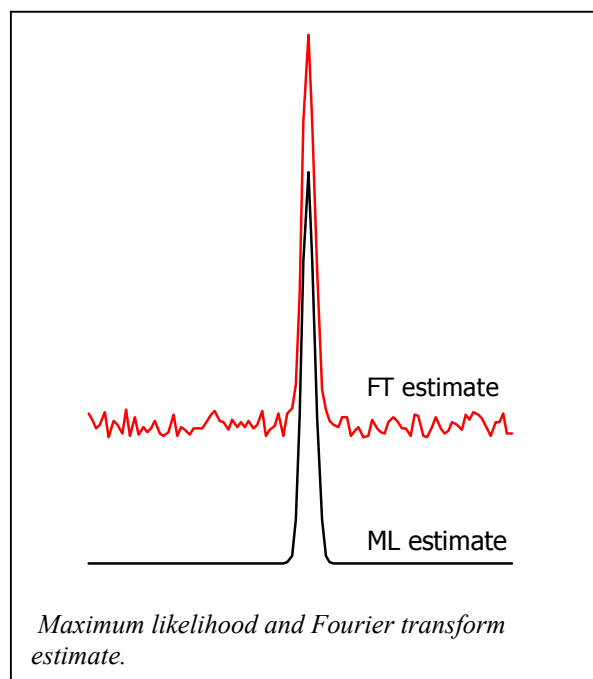
Approach: A recent study shows the promise of an alternative method for deriving the spectrum from an interferogram, distributing the noise at the frequencies where it belongs. By employing “Maximum Likelihood Inversion” [Bialkowski, Appl. Spectrosc. 52, 591 (1998)], we are working to achieve adequate accuracy and dynamic range for practical optical isotope ratio measurement. This program pivots on the implementation of an expectation-maximization (EM) implementation of Maximum Likelihood (ML) Inversion, enabling dynamic range enhancement of line emission spectra. The published algorithm has been implemented and tested with small data segments on a desktop computer. The algorithm, particularly scalable to multiple processors, has been ported to a parallel architecture. Preliminary experiments have been performed to validate the parallelization. Because the computation of this inversion is costly, several strategies have been identified to effectively scale the approach to complete data sets.

Results and Future Plans: Scalability studies indicated excellent performance for the parallel implementation of the algorithm, with minimal loss in performance from inter-processor communication. The parallel implementation is portable between parallel computers, using standard libraries. Convergence performance was poor, and precluded inversions of even moderate resolution spectra.

Three technical approaches have been identified to achieve practical transform times with this iterative algorithm:

- region-of-interest identification and fitting
- filtered initial parameter estimation
- application of an accelerated EM algorithm.

Collaboration with scientists in the High-performance Computing and Statistical Engineering divisions has and will continue to be of utmost importance for further progress.



4. Improvement of Instrumental Performance in the Presence of Drift

M.L. Salit, S. Christopher, M. Epstein, G.C. Turk, and M.R. Winchester

Objective: To demonstrate the broader applicability of the Salit-Turk drift correction procedure for improving the precision of analytical measurements.

Problem: Low-frequency noise—often termed drift—results in a poor signal-to-noise ratio for repeated measurements of a given sample and is a common problem for analytical instruments. In 1998, Salit and Turk published an innovative strategy to overcome drift that used all the data in an experiment to create a model of the instrument drift response function. This new approach gave more than 10-fold improvements for precision in ICP-OES measurements. The authors speculated that the method would have general utility for precision chemical metrology and this speculation has now been verified in our laboratory using several analytical techniques, including glow discharge optical emission spectrometry (GD-OES) and atomic absorption spectrometry (AAS).

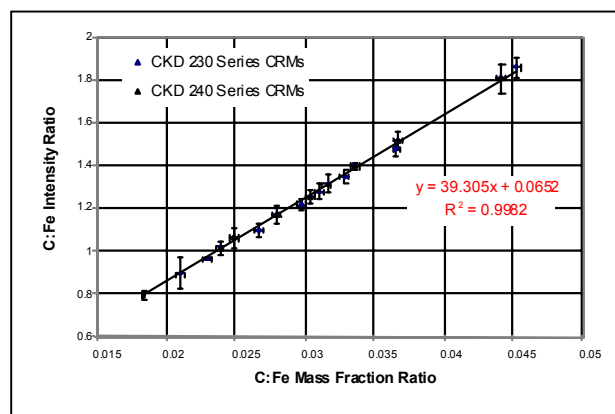
Approach: Drift correction methods that are usually used in GD-OES assume that calibration (and recalibration) can be done in a time frame that is short enough to be unaffected by drift. However, rigorous calibration in GD-OES—spanning a range of calibrants, repetitively measured—is time intensive. Drift does occur, compromising the validity of the calibration and possibly introducing analytical bias into the process. One type of drift that is observed in GD-OES is a burn-to-burn (sample-to-sample) variation of instrumental sensitivity and background. This drift can be caused by reduction of light transmission by the window that separates the glow discharge cell from the vacuum spectrometer.

The method's effectiveness for compensation of drift-induced calibration bias was tested by the determination of C, P, S, and Si in grey cast iron, using 17 CRMs as calibration samples. This analysis accentuated the problem—because of the time per sample and intense conditions required, the vacuum wavelengths measured, and the number of calibrants included.

The drift-corrected, carbon calibration data are graphed above. The well-defined calibration line illustrates the significant improvement that was achieved.

Experiments demonstrating the application of the Salit-Turk drift correction procedure in AAS, both flame and cold vapor, also have been done. In flame AAS, Cu, Fe, and Zn were determined in SRM 909 Human Serum using a dynamic dilution sample introduction pump system and internal normalization with Mn. Precision improved by factors between 3-6 for the elements measured. The procedure was applied in cold vapor AAS determination of Hg in Dust, SRM 2584. A drift of about 13% was observed over 5 hours of data collection, yet the relative precision for each sample ranged from 1-4% (1s). The Hg concentration determined in this material was 5.25 ppm (mg/kg) with a between sample relative standard deviation of 1.7%.

Results and Future Plans: The application of the drift correction methodology has improved the quality of NIST measurements, as noted above. The larger impact that can be achieved by its adoption and use outside NIST is also being promoted. Significant progress has been made in its transfer to the broader analytical community. Joint experiments have been done with both primary and secondary reference material providers in the U.S. and abroad; a successful collaboration has been completed with another agency of the U.S. government; and, several co-operative arrangements, both formal and informal, have been developed with analytical instrument



manufacturers.

5. New Analytical Methodologies for Environmentally Significant Organic Species

M.M. Schantz, W.W. Brubaker, Jr., S.Tutschku, and S.A. Wise

Objective: To develop analytical methodologies for the quantification of methylmercury, organotins, and non-*ortho* polychlorinated biphenyls (PCBs) in natural matrices.

Problem: Analytical methodologies are well established for measuring *ortho*-substituted PCB congeners in natural matrix samples. The non-*ortho* PCB congeners, however, are potentially the most toxic and also generally the lowest in concentration. Because of coelution between the non-*ortho* PCB congeners, PCB 77, PCB 126, and PCB 169, and other chlorinated compounds found in natural matrix samples, an isolation step is needed to separate the non-*ortho* PCB congeners. Likewise, the speciation analysis of mercury and tin compounds has been of interest for some time since the organic forms are the most readily available to living organisms. The analysis of these species requires a selective extraction and analysis method.

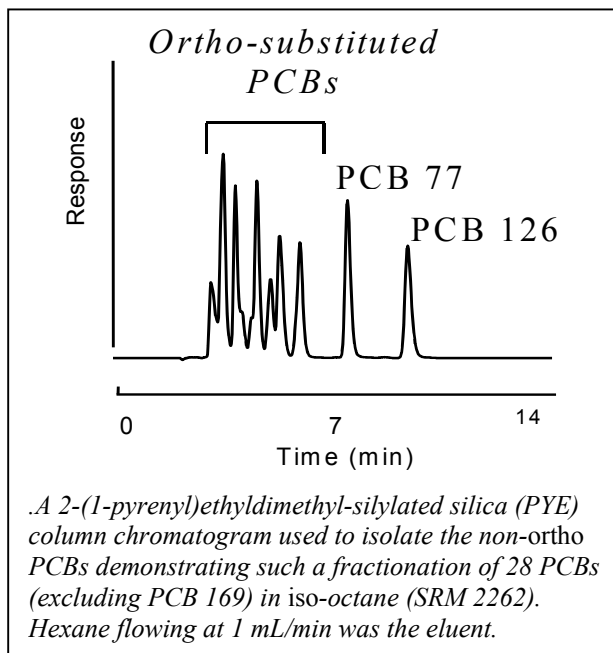
Approach: New methods have been developed for measuring non-*ortho* PCBs and methylmercury in natural matrices and used to determine concentrations of the non-*ortho* PCBs in four SRMs: SRM 1588a, Organics in Cod Liver Oil, SRM 1945, Organics in Whale Blubber, SRM 1944, NY/NJ Waterway Sediment, and SRM 2974, Organics in Freeze-dried Mussel Tissue (*Mytilus edulis*). A known weight of sample was spiked with carbon-13 labeled analogues of the non-*ortho* PCBs and extracted and cleaned-up using the methods typically used for the analysis of these SRMs for PCBs. The additional step for isolation of the non-*ortho* PCBs from the *ortho*-PCBs is illustrated in the figure. Final analysis was done using gas chromatography/mass spectrometry with both electron impact and negative chemical ionization capabilities.

A new analytical procedure for methylmercury has been developed using microwave digestion in acidic media followed by phenylation and solid phase microextraction (SPME) with final analysis using gas chromatography with atomic emission detection (GC-AED). The use of SPME is critical as a PCB

concentration step in the measurement of the low level of methylmercury in most natural matrices, and the AED is very sensitive and selective for mercury. Concentration of methyl-mercury in two tissue reference materials: SRM 2977 (Mussel Tissue-Organic Contaminants and Trace Elements) and SRM 1566b (Oyster Tissue) has been determined.

Results and Future Plans: Data for the non-*ortho* PCBs were compared to data available in the literature for these SRMs to validate the new analytical method. Results will be provided as reference values updating Certificates of Analysis. Methylmercury data from the SPME GC-AED method were compared to results from two other laboratories using analytical procedures different from the NIST procedure. All results were in excellent agreement, thereby validating both the new NIST procedure and the methods used by the other two laboratories to provide the literature data. These results have been statistically combined to assign a certified concentration for methylmercury in SRM 2977 (36.2 ± 1.7 ng/g dry mass basis) and SRM 1566b (13.2 ± 0.7 ng/g dry mass basis).

Methodology will be developed for dibenzo-*p*-dioxin and dibenzofuran congeners, as well as tin species, e.g., tributyltin, in existing natural matrix environmental SRMs. The methods developed for the non-*ortho* PCBs and methylmercury will provide starting points to develop appropriate



methods.

6. The Microanalytical Laboratory

L.E. Locascio, M. Branham W.A. MacCrehan, and M.L. Gaitan (812); and J. Xu and C. S. Lee (Univ. of Maryland)

Objective: To develop methods for monitoring and characterizing microchannels and microfluid flow.

Problem: The concept of the microanalytical laboratory continued to grow rapidly in the last year with more than one new product on the market and many more on the way that integrate microfluid components. The majority of new products are being fabricated in quartz substrates since much of the necessary research has been conducted in this material allowing for a shorter laboratory-to-market time. There is much less known about plastic materials in terms of fabrication and micro-channel characterization. In the first year of our competence effort, we have focused on understanding and characterizing flow and surface chemistry in plastic channels fabricated by NIST imprinting methods.

Approach: The process used to fabricate plastic microfluid devices can influence the surface charge on the microchannel wall as has been demonstrated for laser ablated channels. The surface charge and charge density on the channel wall are critical issues in microfluidics since both the rate and direction of electro-osmotic flow are a function of wall charge. Wall charge also controls the adsorption of chemical and biochemical species. We have previously characterized the surface charge associated with our plastic microchannel devices by monitoring the electro-osmotic bulk flow using the current monitoring technique. This method has been used to successfully evaluate flow in plastic microchannels. However, it provides no direct information on the location and density of surface charge in fluid channels. In the past year, we have developed methods to probe the surface of imprinted channels with fluorescent chemical labels that enable the identification of specific chemical groups. We refer to this process as chemical mapping. With chemical mapping, we can determine the effect of our imprinting procedure on the channel charge and can alter our fabrication protocols to modulate this charge. Another drawback associated with the current monitoring technique is that flow measurement is not performed continuously. Because of this limitation, the current monitoring technique cannot be used to

detect changes in flow during the course of an experiment that may be caused by analyte adsorption or fluctuation in the source pump rate. To address this problem, we have been developing methods for integrating silicon elements for flow monitoring and control within our plastic microfluid devices.

Results and Future Plans: Labeling of imprinted PMMA micro-channels with group-specific fluorescent probes indicated that mechanical stress induced the formation of carboxylate moieties that were concentrated in the channel walls and in surface defects. Non-imprinted materials and the channel floors did not reveal significant amounts of carboxylate or amine functional groups. Proteins were preferentially adsorbed to the negatively charged channel walls as compared to the floor as shown in the figure. The formation of carboxylate functionalities in the PMMA using the imprinting techniques will likely alter the adsorptive and electro-osmotic properties of the polymer microchannels. Integration of silicon components with plastic microfluid channels for flow monitoring has also been a focus of our research. Microheating elements fabricated in silicon have been successfully coupled to polymer channels. Preliminary results show that these devices can be used to continuously monitor fluid flow in integrated microfluid devices. Future work will focus on chemically modifying the microchannel walls to alter channel charge for fluid control for flow stability. We will also attempt to implement

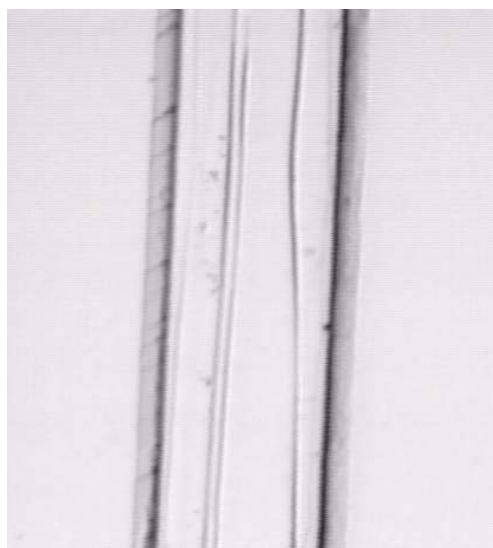


Image of Microfluid Channel with Carboxylate-specific probes.

microheaters in microfluid systems for flow control with feedback.

7. *New Infrared Spectral Database Introduced to Support Remote Sensing Applications*

P.M. Chu, F.R. Guenther, P.A. Johnson, G.C. Rhoderick, and W.J. Lafferty (844)

Objective: To develop a “Quantitative Infrared Database” to support open-path Fourier transform (FT) infrared measurements of chemical emissions and hazardous air pollutant (HAP) molecules.

Problem: Over the last decade, growing concerns about the environment in general and air quality in particular have stimulated the development of improved, cost-effective field monitoring methods. With FT infrared-based technologies multiple airborne chemical contaminants can be measured simultaneously – because each molecular species has a unique infrared spectrum—at part-per-billion level sensitivities. The *in-situ* and real-time nature of this approach offers several advantages over traditional point source monitoring techniques for applications such as determining fugitive emissions and chemical contaminants from industrial processing plants, hazardous waste and municipal landfills, water treatment plants, oil refineries, and chemical plants. Following successful testing of FT infrared methods during remediation of several Superfund sites, the US Environmental Protection Agency (EPA) has issued a protocol (TO-16) for FT infrared open-path remote sensing. Successful implementation of this protocol is highly dependent on the availability of high-quality reference spectral data from a definitive source since molar absorptivity data in the literature widely differ.

A validated quantitative database traceable to national measurement standards is a critical part of the infrastructure required for establishing emerging infrared-based monitoring technologies. New infrared-based technologies coupled with the NIST spectral database provides both industry and EPA with a tool for assessing regulatory compliance that is both cost effective and less invasive.

Approach: SRD 79 data are based on NIST primary gravimetric standards prepared with starting materials of assessed purity and procedures that minimize contamination. For each compound, the absorption coefficient spectrum was calculated

using nine transmittance spectra and the Beer’s law relationship. The uncertainties in the absorption coefficient data were estimated from the linear regressions of the data and considerations of other error sources such as the non-linear detector response. For absorption coefficient values greater than $1 \times 10^{-4} (\mu\text{mol/mol})^{-1} \text{ m}^{-1}$, the average relative uncertainty is 2.2 %. Intercomparisons with a number of expert laboratories, including the National Physical Laboratory of the UK, were used to assure the quality of the NIST data.

Results and Future Plans: Absorption coefficient data for 21 high priority HAPs on a US EPA priority list has been published as the NIST Standard Reference Database (SRD) 79, version 1.00. Data for ten additional compounds will be available shortly. The data are stored in the standard JCAMP-DX format to enable universal access to the data. The 0.12 cm^{-1} resolution data were processed to generate data at a number of different resolutions and apodizations to provide users with data that closely match their experimental parameters. A digital signature accompanies each data file, allowing users to ensure the integrity and source of the data file and traceability to NIST.

This quantitative infrared database is an ongoing project at NIST. Additional spectra will be added to the database as they are acquired and updates will be available over the Internet. Plans include continued data acquisition for the compounds listed in the 1990 US EPA Clean Air Act Amendment, as well as for those compounds that are of concern in global warming and emissions trading. Additionally, inter-comparisons of NIST primary standards and molar absorptivity data with National Metrology Institutes will be expanded to facilitate the use of this database in issues of global interest and impact.

Publications:

Chu, P.M., Guenther, F.R., Rhoderick, G.C., Lafferty, W.J., and Phillips, W.J., “*Sample and Data Processing Considerations for the NIST Quantitative Infrared Database*,” Proc. SPIE, 3534, 204 (1998).

Chu, P.M., Guenther, F.R., Rhoderick, G.C., and Lafferty, W.J., “*The NIST Quantitative Infrared Database*,” J. Res. Natl. Inst. Stand. Technol., 104, 59 (1999).

8. *A Henry's Law Constants Database for Environmentally Significant Compounds*

D.L. Poster, M.M. Schantz, H.A. Bamford, and J.E. Baker (Univ. of Maryland)

Objective: To review critically and measure Henry's Law constants for environmentally significant compounds.

Problem: Physical property data for many hazardous organic contaminants listed in the U.S. EPA's Clean Air Act Amendment of 1990 are required by a wide range of communities, including those involved with (a) implementing environmental clean-up programs, (b) modeling the fate and distribution of organic compounds in the environment, and (c) assessing human health and environmental effects associated with exposure to pollutants. However, physical property data of organic contaminants are lacking or largely inadequate for estimating their environmental behavior. Large portions of physical constant data are suspect because reported values were made at lower levels of sophistication than available today.

Approach: A physical property database for environmentally significant compounds will consist of data obtained from the literature and from measurements. The literature review will collect references that contain information on physical constants such as, surface area, heat of fusion, entropy of fusion, aqueous solubility, vapor pressure, and Henry's Law constant, and will document the measurement techniques used. One hundred twenty two references are reviewed for a wide range of compounds (Table 1). Reported values and the methods used to derive these values are extracted. Only references that contained data resulting from direct measurements are tabulated. Papers that replicate data from primary sources, are listed in the bibliography of the review. In the data compilation, each compound's Chemical Abstract Service number, molecular weight, physical constant value, method of measurement, and temperature of measurement are listed. Laboratory measurements were conducted to assess data for a range of PAHs and PCBs. Henry's Law constants were measured with equilibrium methods using assays with sufficient sensitivity for infinitesimally dilute solutions of contaminants. Simultaneous measurements of gaseous and dissolved concentrations near those found in the environment were made. Investigations of the temperature

dependence of Henry's Law constants quantified temperature effects on the air-water distribution of 13 PAHs and 24 PCBs. The temperature dependence of the Henry's law constant for each compound is modeled using the van't Hoff equation to calculate the enthalpy and entropy of volatilization. These data can be used to extrapolate the Henry's law constants within the experimental temperature range, a unique part of this work. The experimental temperature range chosen represents temperatures within environmental systems.

Table 1. Physical Property Database Compounds	
Compound Class	Number of Compounds
Polycyclic aromatic hydrocarbons (PAHs)	33
Chlorinated aliphatic compounds	19
Polychlorinated biphenyl congeners (PCBs)	152
Chlorinated benzenes	13
Polychlorinated dinbenzo-pdioxins	16
Polychlorinated dibenzofurans	56

Results and Future Plans: This physical property database contains 289 organic contaminant compounds. Henry's law constants for 13 PAHs and 26 PCBs have been experimentally determined between 4°C and 31°C. These data represent the first experimentally measured temperature dependence of the Henry's law constant for 9 of the 13 PAHs and 24 of the 26 PCBs. After using relationships between temperature and the Henry's law constants for interpreting the thermodynamic relationship between the enthalpy (ΔH) and entropy (ΔS) of phase change for these compounds, this program will be concluded.

Publications:

Bamford, H.A., Poster, D.L., Baker, J.E. 1999. *Method for measuring the temperature dependence of the Henry's law constant of selected polycyclic aromatic hydrocarbons. Polycyclic. Aromat. Compd.* In Press.

Bamford, H.A., Poster, D.L., Baker, J.E. 1999. *Temperature dependence of the Henry's Law Constants of Thirteen Polycyclic Aromatic Hydrocarbons Between 4°C and 31°C.* Environ. Toxicol. Chem., 18:1905-1912

Bamford, H.A., Baker, J.E., Poster, D.L. 1998. *Review of methods and measurements of selected hydrophobic organic contaminant aqueous solubilities, vapor pressures, and air-water*

partition coefficients. NIST Special Publication 928, Gaithersburg, MD.

9. An Update to NRLXRF and NBSGSC – Fundamental Parameters in X-Ray Fluorescence Spectrometry

*J.R. Sieber and W.T. Elam (Naval Research
Laboratory)*

Objective: To bring up to date the landmark X-ray fluorescence (XRF) fundamental parameters computer programs NRLXRF (1978) and NBSGSC (1985). To update atomic parameters published since 1985 and to include an improved calculation of the spectrum from an X-ray tube. To publish this new database, to allow its critical evaluation and use.

Problem: XRF analysts apply fundamental parameter (FP) software to improve accuracy when they have few calibration standards. The programs NRLXRF and NBSGSC have served this purpose for over 15 years and still are requested, even though their algorithms, data files, and programming codes are significantly dated, limiting important applications, especially for custom spectrometer development. Commercial software developers have not adopted a standardized database form for the fundamental parameters and do not provide source codes that can easily be modified for research.

Approach: The fundamental parameters method relies on the use of equations that express the intensity of X-ray emission in terms of parameters that are independent of a particular sample. These parameters fall into two categories: instrument parameters and atomic parameters. Instrument parameters can be measured or are known *a priori*. The remaining parameters are associated with the elements of which the sample is composed and describe the X-ray properties of these elements. The properties of the elements together with the elemental composition of the sample can be used to compute the expected X-ray emission of the sample. The computations can be iterated to determine the composition of an unknown sample. The accuracy of the atomic parameters is crucial to the accuracy of the FP method. In particular, X-ray absorption cross-sections contribute directly to the quality of the results. Other parameters, e.g., Coster-Kronig transition probabilities, produce smaller effects and high accuracy is not required.

However, the more accurate the parameters, the more useful the calculations will be and the greater the accuracy that can be achieved.

Table 1. Fundamental parameters required for calculations in XRF. Parameters are needed for each element in a sample

Atomic number	Photoabsorption cross-section
Atomic weight	Coherent scattering cross-section
Pure element density	Incoherent scattering cross-section
X-ray absorption edges:	Coster-Kronig transition probability:
Energy	X-ray emission lines
Jump ratio	Energy
Fluorescence yield	Relative intensity

The authors undertook to produce a consistent set of parameters optimized for FP calculations using values available in the literature. The required parameters are given in Table 1. The newer and more complete IUPAC notation is used for X-ray emission lines. The calculation of spectra from X-ray tubes was based on recent work in electron microprobe analysis. The fast and versatile FP algorithm from NRLXRF was used because it handles mixtures of compounds and particulate samples rather than simple elemental compositions and it can be extended to multilayer samples by using the analytical solutions to Sherman's equations derived by De Boer.

Results and Future Plans: The results of this work, in the form of both a database and computer source code, will be made available to the public and to commercial XRF software developers. At present, the computer codes are nearly ready to perform the first FP calculations of intensity from samples to verify the output of the code and check for improvements in accuracy with the new parameters. Modifications for particulate and multilayer samples are planned. Finally, a graphical user interface will be added to the program as time permits.

10. Real-Time Characterization of Lithium Transport in Thin Films

G.P. Lamaze and H. Chen-Mayer

Objective: To measure lithium concentration and mobility in thin multilayer films in real time.

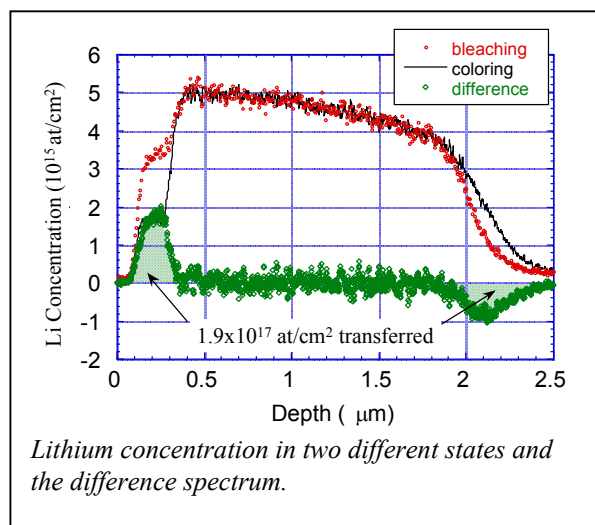
Problem: Lightweight, less toxic lithium-based batteries now dominate the market for laptop computer, cell phone and other consumer electronics. Market demand for all types of rechargeable cells is expected to grow at a compound rate of 11 per cent per year, reaching a total of 2 billion cells by 2001 of which the lithium ion cell share is expected to be 440 million cells. Thus the market for lithium ion cells will soon reach about \$4 billion. In spite of this rapid commercialization, much of the underlying materials science is not completely understood. In these systems, a single ion species is shuttled back and forth between anode and cathode on charge and discharge. NDP can be used to examine the lithium distribution in anode and cathode materials to try to explain such problems as charge capacity loss with cycling, lower than theoretically attainable reversible charge capacity, and less than theoretically attainable maximum charging and discharging current densities.

Approach: First studies were undertaken with lithium electrochromic devices, which are similar to lithium batteries in both construction and operation. Samples are placed in a cold neutron beam at the Center for Neutron Research reactor. The lithium profiles are deduced based on the measurement of the energy of alpha particles from the ${}^6\text{Li}(n,\alpha){}^3\text{H}$ reaction. The alpha particles pass through the layers and lose energy through interactions with the matrix. The residual energy of the particles is measured with surface barrier detectors. Because the starting energy of the alpha particles is fixed, the energy loss is obtained by a simple subtraction. This measured energy loss, when combined with a calculated energy loss per unit depth (dE/dx), provides the depth of the originating lithium nucleus. In this case, *in situ* measurements are taken with different bias voltages on the film layers. The bias causes the lithium to migrate between different layers while changing the optical transparency of the film. The profiling technique is non-destructive allowing repeated cycling of the device. The real time nature of the NDP measurement process

allows us to watch changes in transparency as the lithium migrates between layers.

Results and Future Plans: The figure shows a typical profile obtained for lithium profile measurements of multilayer films. The small circles represent the device in its bleached state and show that most of the lithium is concentrated in the counter electrode (CE) and the ion conductor (IC). The small diamonds represent the device in the coloring state. In the colored state, the profile shows that lithium is primarily localized in the IC and the WO_3 though some lithium remains “bonded” in the CE. Among the information learned in this study was critical process chemistry, migration of lithium into inactive layers, and lithium loss from active layers during accelerated life tests.

We have begun the application of this technique to the study of another lithium single-ion conductor systems, i.e., “rocking chair” batteries. With Tufts University, we have measured lithium content and lithium/cobalt ratios in LiCoO_2 , a material that can be used as an electrode material in lithium batteries. The lithium content is measured by neutron depth profiling while the cobalt content is measured by neutron activation analysis. We plan to continue our collaboration with Tufts and expand our work in the area of battery technology.



11. SRMs to Support Chemical Measurements in Industrial Applications

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Objective: To promote U.S. economic growth by working with industry to develop and apply measurements and standards.

Problem: The development of new technology and products, coupled with the evolution and advancements of analytical instrumentation used by industry, results in an ever-expanding need for standards. The Division balances its broad program in compositional and chemical standards among continuously produced standards (e.g. primary materials), renewals (previously certified materials), and new standards. The Division works with broad-based industrial groups to identify and produce new standards—which typically will require the development of new analytical methodology or refinement of existing methodology—research in analytical methods.

Approach: New standard activities reside in all functional areas and Groups of the Division. Each project has its own unique characteristics, but each also has common stages: an indication of need by some industry advocacy group; the development and definition of NIST capabilities; and, then, the application of these NIST capabilities in value assignment of a material available for broad distribution as an SRM.

Results and Future Plans: Five examples of on-going projects are provided to illustrate the breadth of industrial measurement problems being addressed by the Division.

SRM 2035/2035a Near Infrared Wavelength: NIR spectroscopy is a technique widely used in process control for a variety of industries. Through interactions with two committees of ASTM the need for optical filter wavelength standards in this wavelength region was established. In addition, technical workshops and meetings were held with users and regulators to refine these needs. Several prototype materials were evaluated; a round robin to potential end users in the chemical, polymer, pharmaceutical, and analytical instrumentation

industries were completed. Technical issues such as homogeneity, temperature and environmental stability, polarization and bandwidth effects required investigation. The first material has now been certified.

SRM 861, Aerospace Superalloy: The U.S. aerospace industry is a leading technology driver in R&D spending and the nation's leading net exporter of manufactured products. The aircraft industry and supporting foundries and their Consortium on Casting of Aerospace Alloys brought to NIST the need of the industry to produce turbine blades with sulfur concentrations near 1 mg/kg, a critical level between acceptable and unacceptable materials. Presently, the two established techniques used by industry to measure sulfur are discordant and both require standards for calibration and validation—standards that did not exist. The Division has investigated the extension of its primary isotope dilution mass spectrometric method to the low concentration required, accounting for the variability of the blank, the limiting source of uncertainty in this measurement. A material has been prepared to benchmark the need and NIST's measurement capability. Preliminary results indicate that the certified sulfur value will be an order of magnitude lower than any other standard.

SRM 2721/2722 Moisture in Crude Oil: The measurement of moisture in crude oils is important for the oil industry because of the large amount of crude oil that is recovered by a steam process and shipped saturated with water. ASTM methods existed for this measurement; however reference materials do not exist to benchmark the accuracy of these methods, or to gauge their robustness across materials and conditions. In preparation for certification, these methods have been critically assessed and sources of systematic bias have been enumerated. One result was the identification of a large negative bias for the recommended ASTM method D1533 if the oil is not completely dissolved or if the instrument is not properly calibrated. The development of a reliable method has resulted in moisture certification in two different crude oil materials at approximately 926 and 96 mg/kg. It is also intended to certify these two materials for their sulfur content, another chemical component that strongly affects crude oil value.

Hydrogen in Titanium Alloys: Hydrogen is one of the chief contributors to brittleness in metals; its

measurement and control in certain alloys is critical, especially for the aerospace and nuclear power industries. The principal method used in industry to measure hydrogen is calibrated with working standard materials. At one time NIST used this method and certified materials in co-operation with industry. However, NIST no longer supports either this technique or the mode of certification where no NIST measurements are included. The ASTM metals standards committee has steadfastly maintained the importance of benchmarking this measurement. Thus, a method has been developed that can produce metal standards of absolutely known hydrogen concentration. This method is based on the controlled reaction of hydrogen with titanium. Homogeneity is checked by neutron incoherent scattering and concentration is verified by cold-neutron prompt-gamma activation analysis. The first material has been prepared near the critical level of 100 mg/kg. In addition, new materials will be prepared at two bracketing levels.

SRM 1848 Lubricant Additive Package: The lubricants industry is estimated to be worth \$5 billion in the United States. Although ASTM maintains a range of analytical methods for lubricants, none of the methods have bias statements, and there are no certified reference materials to verify the accuracy of analysis. Thus, a SRM certified for additive elements in passenger car motor oil was proposed to fill the need for traceable standards for this industry, and this standard is in the process of being certified in co-operation with industry laboratories. The candidate material was donated by one of the major U.S. producers, its homogeneity checked at NIST, and a round robin of major industry laboratories has been conducted. Quantitative procedures for XRF analysis have been implemented at NIST to benchmark established NIST and industry instrumental methods. At NIST, certification measurements for 8 elements, B, N, Mg, P, S, Cl, Ca, and Zn, by nuclear methods, XRF, atomic spectroscopy, and mass spectrometry are in progress. The goal is to achieve uncertainties for the NIST certified values of 0.5-1.0% to meet the industry's need (~3%).

12. SRM Activities to Support Nutritional Labeling

K.E. Sharpless, J. Brown Thomas, S.A. Margolis, C.S. Phinney, L.C. Sander, L.T. Sniegowski, L.K. Walton, and L.J. Wood

Objective: To develop food-matrix Standard Reference Materials (SRMs) to support nutrition labeling issues.

Problem: The Nutrition Labeling and Education Act (Public Law 96-359) requires that specific nutritional information be provided on all processed foods sold in the U.S. In a recent study by the U.S. Food and Drug Administration, the accuracy of label information ranged from 98% to 54% for nutrients for which labeling is required. As more food-matrix SRMs become available, label accuracy should improve when the food and nutrition communities employ these food-matrix SRMs in their analyses. Food-matrix SRMs are needed to validate analytical methods and for quality assurance when assigning concentration values to in-house control materials. Such reference materials will facilitate compliance with new nutritional labeling laws, provide traceability for food exports needed for acceptance in many foreign markets, and improve the accuracy of nutrition information that is provided to assist consumers in making sound dietary choices.

Approach: AOAC International has developed a nine-sectored triangle in which foods are positioned based on their fat, protein, and carbohydrate content. AOAC's belief is that one or two reference materials within each sector should be representative of other foods within that sector and could be used for quality assurance and method validation when analyzing those other foods. NIST does not have the resources or analytical capabilities necessary to measure all of the analytes for which labeling is required; therefore, nutrient concentrations in SRMs and RMs have been determined through collaborations with the food industry and food-related government regulatory agencies. Certified values are provided for analytes for which NIST alone (using two independent methods) or NIST and collaborating laboratories provide data. Reference or information values are provided for analytes for which only collaborating laboratories provide data.

Results and Future Plans: NIST is actively working to provide an increased array of SRMs with values assigned for proximates (procedurally defined values for fat, protein, carbohydrate, etc.), fatty acids, cholesterol, vitamins, elements of nutritional interest, etc. SRMs and RMs are now available or are in preparation for the sectors in the AOAC triangle shown.

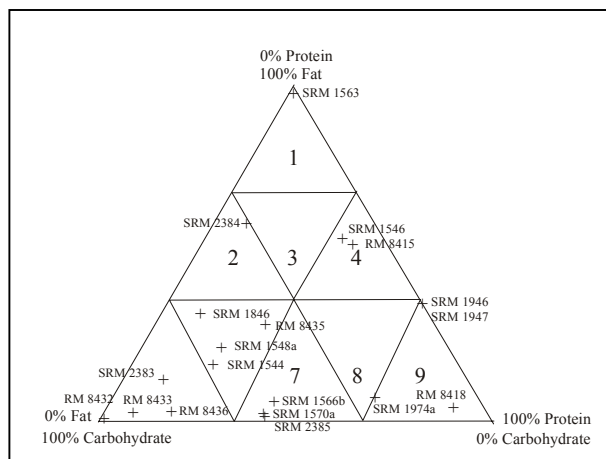
In 1998, NIST certified SRM 1546 Meat Homogenate, a canned meat product containing ham, pork, and chicken. This material was developed at the request of U.S. Department of Agriculture's Food Safety Inspection Service. Concentration values were assigned based on values from NIST, from an interlaboratory comparison exercise involving 17 member laboratories of the National Food Processors Association's (NFPA's) Food Industry Analytical Chemists Subcommittee (FIACS), and from several additional collaborating laboratories. Concentration values have been assigned for proximates, cholesterol, individual fatty acids, water-soluble vitamins, and elements of nutritional interest.

Using data provided by collaborating laboratories, values have been assigned for proximate concentrations in ten existing SRMs and RMs: SRM 1563 Cholesterol and Fat-Soluble Vitamins in Coconut Oil (Natural and Fortified), SRM 1566b Oyster Tissue, SRM 1570a Spinach Leaves, SRM 1974a Organics in Mussel Tissue (*Mytilus edulis*), RM 8415 Whole Egg Powder, RM 8418 Wheat Gluten, RM 8432 Corn Starch, RM 8433 Corn Bran, RM 8435 Whole Milk Powder, and RM 8436 Durum Wheat Flour. (Most of the materials in this group previously had values assigned only for concentrations of inorganic analytes of nutritional or toxicological interest.)

SRM 2384 Baking Chocolate and candidate SRM 2385 Spinach are currently in preparation. These materials were developed as a result of a workshop held at NIST in 1997 in which SRM needs of the food industry were identified. Materials in sectors 2 and 7 of the AOAC triangle and a vegetable material with values assigned for persistent pesticides were the top three priorities identified. SRM 2384 Baking Chocolate lies in sector 2 of the AOAC triangle; with the assistance of NFPA's FIACS, values will be assigned for proximates, individual fatty acids, total dietary fiber, caffeine, theobromine, several water-soluble vitamins, and

elements of nutritional interest. Candidate SRM 2385 Spinach lies in sector 7 of the AOAC triangle. (This material will be a canned material, unlike SRM 1570a, which is freeze-dried and finely-ground spinach leaves.) NIST-specified pesticides will be applied to candidate SRM 2385 at normal application rates when it is grown. The material is expected to have values assigned for proximates, individual fatty acids, total dietary fiber, elements of nutritional interest, vitamins, carotenoids, folates, and pesticides.

Recently we held a food-related reference materials needs assessment workshop at the AOAC meeting in Houston, TX with broad representation from the food, nutrition, and regulatory communities. High priority needs identified at the workshop include SRMs for nutraceuticals, allergens such as peanut proteins, additives and preservatives, juice authenticity, chondroitin sulfate, and moisture in grain, as well as a sugar standard for use as a calibrant. Future division activities in the food/nutritional area will be driven by this input.



13. SRM Activities to Support Health-Care Measurements

J. Brown Thomas, D.M. Bunk, S. Christopher, J.J. Dalluge, D.L. Deuwer, S.E. Long, E.A. Mackey, M.S. Rearick, K.E. Sharpless, L.T. Sniegowski, S.Tutschku, R.D. Vocke Jr., M.J. Welch, and W.E. May

Objective: To provide certified reference materials that support measurement accuracy and traceability for laboratories performing health-related measurements and In-vitro Diagnostic Device (IVDD) manufacturers.

Problem: Inaccuracy in health-related measurements raises overall health care costs, results in misdiagnoses, and leads to inaccurate conclusions in clinical studies. In addition, lack of certified reference materials (CRMs) hampers traceability, and with the new European Community IVDD directive which will require traceability to “standards, of the highest metrological order” there is an urgent need for new health-related SRMs.

The European Community (EC) has scheduled full implementation of a directive on in vitro diagnostic Devices (IVDD) for December 2003. The directive requires all manufacturers of IVD products sold in Europe to have an “EC Stamp,” verifying that they comply with the conditions of the directive. U.S. companies are major exporters of IVDD products to European markets, and thus are directly affected by the directive. One of the major components of this directive is a requirement that products are traceable to “standards of the highest order,” e.g., nationally/internationally recognized certified reference materials (CRMs). At present, neither CRMs nor reference methods are available for most of the several hundred analytes that are measured in medical laboratories. These analytes fall into two classes: “A list” analytes that are well-defined chemical species of which there are approximately 80 and “B list” analytes that are less well-defined and number in the hundreds.

One mechanism available on a limited basis for providing the necessary traceability is using clinical reference laboratories to establish traceability to higher order methods. Such laboratories are well established in Europe, but analogous laboratories in the U.S. have generally not been economically

viable. With a shortage of clinical reference laboratories in the U.S., it may be difficult for U.S. manufacturers of IVDD products to get the necessary traceability. The European reference laboratory services are very expensive and may not have the reputation to properly address U.S. customer needs. From discussions with representatives of the U.S. IVDD industry, it is clear that they prefer the use of commutable, internationally recognized CRMs as their basis for establishing “traceability to standards of the highest order”.

Approach: NIST works closely with the American Association for Clinical Chemistry (AACC), the Centers for Disease Control and Prevention (CDC) and other organizations interested in health-related standards to prioritize our SRM development activities. In general, most health-related SRMs are a matrix of serum or whole blood with certified concentrations of clinically important analytes that have been identified as priorities. In addition to substances normally found in blood, such as cholesterol or calcium, priorities may include toxic substances such as heavy metals, substances believed to improve health status, such as vitamins and other antioxidants, or markers that signal serious conditions, such as the heart attack marker, troponin-I. Once development has begun for a particular SRM, a variety of certification modes may be used, depending upon the measurement needs and NIST capabilities.

CDC identified a need for a whole blood SRM for toxic metals, specifically lead, cadmium, and both inorganic mercury and methyl mercury. They prepared a two-level material from bovine blood with one level representing normal human levels and the other representing elevated levels. The lead concentrations were achieved through feeding of the cows; the elevated levels of the other analytes were achieved through spiking the collected blood material. Certification measurements for cadmium involved using two independent methods at NIST, ID-ICPMS and neutron activation analysis while total mercury was assayed by CV-AAS and ID-ICPMS. Certification of lead was accomplished using the ID-ICPMS definitive method for lead in blood. Value assignment of the methyl mercury involved NIST measurements using GC-atomic emission detection.

Since first issued in 1989, SRM 968 Fat-Soluble Vitamins and Carotenoids in Human Serum has found widespread use in the clinical laboratory community. The measurements for the third renewal of this SRM (SRM 968c Fat-Soluble Vitamins, Carotenoids and Cholesterol in Human Serum) have been completed. Fat-soluble vitamins and carotenoids were measured using two or more NIST methods involving liquid chromatography, along with liquid chromatography methods used by selected laboratories that participate in the NIST Micronutrients Quality Assurance Program. Cholesterol was measured in SRM 968c using the NIST ID/MS definitive method for serum cholesterol.

Troponin-I is a protein that is released into the blood when heart tissue is damaged. Because elevated levels of troponin-I correlate extremely well with a recent heart attack, physicians are now using troponin-I measurements as a diagnostic tool. Unfortunately, different immunoassays for troponin-I produce widely different results. In one large study, the mean from one system was more than 20 times the mean from another. This analyte was identified by the AACC Standards Committee as their highest priority for development of a reference material. NIST is using liquid chromatography/mass spectrometry and MALDI mass spectrometry to characterize purified preparations of troponin-I that are then subjected to testing in laboratories using a variety of routine assays.

Results and Future Plans: Measurements for the lead, cadmium, and total mercury in SRM 966 are complete, and measurements are underway for methyl mercury. Measurements have been completed for SRM 968c which will have certified values for cholesterol, four vitamins, and two carotenoid compounds. Reference values will be provided for nine additional vitamins and carotenoid compounds and information values will be provided for seven additional species. For troponin-I, twelve materials have been evaluated by NIST for their purity and molecular weight distributions. These materials will be sent to a group of laboratories organized by AACC for measurement by the most widely used methods for troponin-I. Those results will be correlated with NIST results and the material judged best will be chosen as a candidate SRM.

We are committed to support the U.S. IVDD industry by maintaining our existing measurement capabilities and serum-based SRMs for calcium, chloride, cholesterol, creatinine, glucose, lithium, magnesium, potassium, sodium, triglycerides, urea, and uric acid. We also plan to intensify both our in-house research program and our interactions with the medical professional and medical laboratory community to develop matrix-based SRMs for the following clinical diagnostic markers over the next 3-5 years:

- | | |
|-------------------------------|--------------------------------|
| • Troponin | <i>heart attack marker</i> |
| • Homocysteine | <i>risk of heart disease</i> |
| • Glycated Hemoglobin | <i>diabetes status</i> |
| • Cortisol | <i>endocrine function</i> |
| • Thyroxine | <i>thyroid function</i> |
| • Cadmium | <i>heavy metal toxicity</i> |
| • Folic Acid | <i>neural tube defects</i> |
| • Mercury | <i>heavy metal toxicity</i> |
| • Speciated Iron | <i>hemochromatosis, anemia</i> |
| • Human serum Albumin | <i>renal failure</i> |
| • Prostate Specific Antigen | <i>prostate cancer</i> |
| • Thyroid Stimulating Hormone | <i>thyroid function</i> |

14. SRM Activities to Support Environmental Measurements

D.A. Becker, B.A. Benner Jr., S. Christopher, R. Demiralp, M.S. Epstein, J.D. Fassett, T.L. Green, R.R. Greenberg, F.R. Guenther, A.P. Lindstrom, R.M. Lindstrom, S.E. Long, C. Mack, E.A. Mackey, A.F. Marlow, M.C. Mildner, K.E. Murphy, R.M. Parris, B.J. Porter, D.L. Poster, L.C. Sander, M.M. Schantz, J.R. Sieber, G.C. Turk, S. Tutschku, R.D. Vocke Jr., S.A. Wise, L.J. Wood, L. Yu, and R. Zeisler

Objective: To provide Standard Reference Materials with value-assigned concentrations of important toxic constituents. These SRMs serve as quality assurance tools for environmental measurement and monitoring efforts worldwide.

Problem: There are a wide variety of environmental monitoring and research programs in the U.S. Inaccurate analytical results lead to inappropriate actions. Therefore accurate analytical measurements are of utmost importance for facilitating sound environmental decision making. Quality assurance programs to enhance the reliability of analytical data often depend upon the availability of a broad spectrum of different control and Certified Reference Materials with matrices similar to the actual environmental samples analyzed.

Approach: For the past twenty years, NIST has provided a large number of natural-matrix SRMs to serve as accuracy benchmarks for environmental measurement and monitoring activities within the U.S. For many matrix and/or analyte combinations, NIST is the *de facto* source for such materials worldwide. Therefore, we are committed to developing new SRMs as needed, as well as recertifying high priority materials as their stocks are depleted and /or providing additional information for important new classes of analytes in both new and existing SRMs.

Results and Future Plans: Certification of a number of new and renewal environmentally-related SRMs has been completed recently. Several SRMs have been certified for both inorganic and organic constituents including:

- SRM 1944 "NY/NJ Waterway Sediment" with certified and reference concentrations of 52 PAHs, 29 PCB congeners, 11 chlorinated

pesticides, 17 congeners of 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and dibenzofurans, and 28 inorganic constituents;

- SRM 1649a "Urban Dust/Organic" with certified and reference values for 44 PAHs, 35 PCB congeners, 9 chlorinated pesticides, 17 congeners of 2,3,7,8-polychlorinated dibenzo-p-dioxins and dibenzofurans, 32 inorganic constituents, mutagenic activity, particle-size characteristics, total organic carbon, total extractable mass, and carbon composition;
- SRM 2977 "Mussel Tissue - Organic Contaminants and Trace Elements," and "SRM 2976 Mussel Tissue - Trace Elements and Methylmercury" both have values for PAHs, PCBs, chlorinated pesticides, trace elements and methylmercury.

SRMs completed this year with certified or reference values for inorganic constituents include:

- SRM 2584 "Trace Elements in Indoor Dust - Nominal 1 % Lead" certified for As, Cd, Cr and Hg;
- SRM 2579a, a set of 5 Lead in Paint films (certified for lead) with a blank film (the films are also individually sold as SRMs 2570-5);
- SRM 1641d "Mercury in Water," SRM 1630a "Trace Mercury in Coal" which has been value assigned for Hg, Cl and S;
- SRMs 2586 and 2587 "Trace Elements in Soil Containing Lead," which have been certified for EPA priority pollutant elements; and
- SRM 2782 "Industrial Sludge" which has also been certified for EPA priority pollutant elements.

SRMs completed recently with certified or reference values for organic constituents include:

- SRM 2978 "Mussel Tissue (Organic Contaminants - Raritan Bay, NJ)" with values assigned for PAHs, PCBs and pesticides;
- SRM 1650a "Diesel Particulate Matter" with certified and reference values for 44 PAHs, as well as particle size characteristics and total extractable mass; and
- two new diesel particulate-related materials, SRM 2975 "Diesel Particulate Matter (Industrial Forklift)" and SRM 1975 "Diesel Particulate Extract" (which is a dichloromethane extract of the diesel particulate material used in SRM 2975) with certified values for 10-15 PAHs.

The development of a fish tissue material, SRM 1946 "Lake Superior Fish Tissue," is in progress and it will be issued as a frozen tissue homogenate (similar to SRM 1974a and 1945) with certified values for PCBs, pesticides, total mercury, and methylmercury. Other new and renewal environmental SRMs that are currently in progress include SRM 1632c "Trace Elements in Coal" for inorganic constituents; SRM 1566b "Oyster Tissue" which will be certified for elemental content and methylmercury; SRM 2783 "Urban Air Particulate Matter (APM) on Filter for Trace Elements" which contains less than 1 mg of air particulate material per filter and will be value assigned for concentrations of approximately 25 elements; and SRM 270 "Hard Rock Mine Waste" which will be value assigned for EPA priority pollutant elements. The supply of some very popular natural matrix SRMs were recently depleted and renewals are currently in progress. These include: SRM 1632b "Trace Elements in Coal"; SRM 1566a "Oyster Tissue"; SRM 1941a "Organics in Marine Sediment"; and SRM 1575 "Pine Needles".

As part of a new program in support of the externalization of the U.S. Environmental Protection Agency's (EPA) Water Supply and Water Pollution Performance Evaluation (PE) studies program, NIST is preparing a number of new calibration solution SRMs for both organic and inorganic contaminants. For the semi-volatile organic contaminants 25 calibration solution SRMs have been prepared including six different Aroclors in methanol and transformer oil; toxaphene and total chlordane in methanol; chlorinated herbicides in methanol; chlorinated pesticides in acetone; haloacetic acids in methyl-*t*-butyl ether; 2,3,7,8 tetrachlorodibenzo-*p*-dioxin in methanol; endo-thall, glyphosphate, and diquat dibromide in water; chloral hydrate in methanol; carbamates in acetonitrile; and adipate and phthalates in methanol. For the volatile organic contaminants 15 single component calibration solution SRMs have been prepared, all in methanol, at the 1% concentration levels. Six of the solutions have been completed (benzene, toluene, ethylbenzene, *m*-xylene, *o*-xylene, and *p*-xylene (BTEX)). Work on three of the solutions is nearly completed (tetrachloroethylene, carbon tetrachloride, and 1,1,1 trichloroethane), and seven additional solutions have been ampouled and analyses are in progress (1,1-dichloroethene, dichloromethane, 1,2

dichloropropane, 1,2 dichloroethane, 1,2,3 trichloropropane, isopropyl benzene, and *sec*-butylbenzene). Purities of the neat chemicals used to prepare the volatile and semi-volatile solution SRMs have been determined using appropriate techniques (i.e., DSC, GC-FID, GC-MSD, and/or LC), and additional certification measurements will be performed during FY00. Six additional solutions not yet identified are also planned for FY00. Finally one of five multi-component mixtures has been prepared in FY99 at the 2000 µg/mL level in methanol. For the inorganic solutions required for the EPA PE program, we will use the existing Single Element Spectrochemical Solution SRM series, and we have initiated the establishment of an NTRM program (discussed elsewhere in this report) to supply these materials.

15. Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements

W.E. May, R.M. Parris, C.M. Beck II, J.D. Fassett, R.R. Greenberg, F.R. Guenther, G.W. Kramer, and S.A. Wise; and T. E. Gills, J.C. Colbert, R. Getting, and B. MacDonald (Div. 232)

Objective: To develop a document which provides definitions of terms and descriptions of current practices used at NIST for value-assigning Standard Reference Materials (SRMs) for chemical composition and related properties.

Problem: NIST SRMs are used worldwide for providing quality assurance for chemical measurements. Chemical measurements are becoming increasingly important in international trade decisions and addressing healthcare, environmental and safety-related issues. There has been a recent proliferation of commercial and government-based reference material producers and the current ISO definitions for Reference Materials (RMs) and certified Reference Materials (CRMs). For example, a Reference Material is defined as *a material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials [ISO VIM: 1993, 6.13 [7]].* A Certified Reference Material is defined as *a Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence [ISO VIM: 1993, 6.14].* These definitions say nothing about the quality of the measurement science infrastructure that supports the value-assignment process for RMs and CRMs. This causes confusion for chemical measurement analysts worldwide as they attempt to establish increasingly required traceability for their chemical measurements.

Approach: The quality of assigned values for any CRM or RM is based on the existence and application of sound metrological principles and practices to the value-assignment process. It is with this basic premise that we have developed NIST

Special Publication 260-136, “Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements”. This document provides a complete description of the seven modes used at NIST to acquire analytical data for the value assignment of our SRMs and RMs for chemical measurements and links these modes to three data quality descriptors: NIST Certified Values, NIST Reference Values and NIST Information Values.

Results and Future Plans: A NIST Standard Reference Material® (SRM®) is a CRM issued by NIST that also meets additional NIST-specified certification criteria. NIST SRMs are issued with Certificates of Analysis or Certificates that report the results of their characterizations and provide information regarding the appropriate use(s) of the material. A *NIST Certified Value* is a value reported on an SRM Certificate/Certificate of Analysis for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or accounted for

Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements		Certified Value	Reference Value	Information Value
1. Certification at NIST Using a Primary Method with Confirmation by Other Method(s)		✓		
2. Certification at NIST Using Two Independent Critically-Evaluated Methods	✓	✓		
3. Certification/Value-Assignment Using One Method at NIST and Different Methods by Outside Collaborating Laboratories	✓	✓		
4. Value-Assignment Based On Measurements by Two or More Laboratories Using Different Methods in Collaboration with NIST		✓	✓	
5. Value-Assignment Based on a Method-Specific Protocol		✓	✓	
6. Value-Assignment Based on NIST Measurements Using a Single Method or Measurements by an Outside Collaborating Laboratory Using a Single Method		✓	✓	
7. Value-Assignment Based on Selected Data from Interlaboratory Studies		✓	✓	

by NIST. Values are generally referred to as certified when Modes 1, 2, or 3 have been used for value-assignment and all the criteria for that mode are fulfilled. These three modes all require NIST measurements and oversight of the experimental design for the value-assignment process. The uncertainty associated with a certified value generally specifies a range within which the true value is expected to lie at a level of confidence of approximately 95 % if the sample is homogeneous. If significant sample heterogeneity is included, the uncertainty generally represents a prediction interval within which the true values of 95 % of all samples are expected to lie at a stated level of confidence.

A NIST Reference Value (formerly called Noncertified Value) is a best estimate of the true value provided on a NIST Certificate/Certificate of Analysis/Report of Investigation where all known or suspected sources of bias may not have been fully investigated by NIST. Reference values are generally determined using the following modes:

- Mode 2 or 3 is used when there is lack of sufficient agreement among the multiple methods.
- Modes 4, 5, or 6 are used when the intended use of the value by the measurement community does not require that it be a certified value.
- Mode 7 can be used in special cases, e.g., when results are obtained from another national metrology laboratory with whom NIST has historical comparability data for the method(s) used for the specific matrix/analyte combination.

The uncertainty associated with a NIST Reference Value may not include all sources of uncertainty and may represent only a measure of the precision of the measurement method(s).

A NIST Information Value is considered to be a value that will be of interest and use to the SRM/RM user, but insufficient information is available to assess the uncertainty associated with the value. Typically, the information value has no reported uncertainty listed on the certificate and has been derived from one of the following value-assignment modes:

- Results from modes 4, 5, 6, or 7 in which the intended use of the value by the measurement community does not require that it be a certified or reference value, e.g., information about the composition of the matrix such as the value of “total organic carbon” of a sediment material may be useful to the user in selecting an appropriate analytical method.
- The results from modes 4, 5, 6, or 7 lack sufficient information to assess the uncertainty.
- Results are provided from outside NIST as supplemental information on the SRM matrix and are not measurements typically made at NIST but may be of interest to the user.

NIST has met the chemical reference materials needs of U.S. industry and commerce for nearly 100 years. Coupled with the fast pace of technological change and greater measurement needs, the demand for additional quantities and additional specific varieties of reference materials has mushroomed. NIST, by itself, does not have the resources to provide SRMs (exact sample types, unique compound combinations, concentrations, etc.) to meet all these needs. Without a significant shift in paradigm, we will not be able to address future needs for reference materials, neither nationally nor internationally. The establishment of these seven modes for value assignment of NIST SRMs and RMs and communication of their linkage to the three quality descriptors (NIST Certified Values, NIST Reference Values and NIST Information Values) is a critical component of our strategy to produce an increasing number of SRMs and RMs through collaborative efforts with selected expert laboratories and other National Metrology Institutes/Standards Laboratories.

Publications:

“Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements”, National Institute of Standards and Technology Special Publication 260-136, NIST Spec. Pub. 260-136 (November 1999).

16. Formal Programs for Providing NIST-Traceable Reference Materials from Commercial Sources

W.E. May

Objective: To establish formal programs to facilitate the commercial production and distribution of reference materials with a well-defined (and NIST recognized) traceability linkage to NIST.

Problem: Increased requirements for quality systems documentation for trade and effective decision-making regarding the health and safety of the U.S. population have increased the need for demonstrating “traceability-to-NIST” and establishing a more formal means for documenting measurement comparability with standards laboratories of other nations and/or regions. Standard Reference Materials (SRMs) are certified reference materials issued under NIST trademark that are well-characterized using state-of-the-art measurement methods and/or technologies for chemical composition and/or physical properties. Traditionally, SRMs have been the primary tools that NIST provided to the user community for achieving chemical measurement quality assurance and traceability to national standards. Currently, NIST provides nearly 1400 different types of SRMs and in FY98 sold nearly 37,000 SRM units to approximately 5,000 unique customers; approximately 21,000 units of these represent about 850 different types that are certified for chemical composition. NIST does not have the resources necessary to--by itself--provide the increasing quantities and specific varieties of certified reference materials (exact sample types, unique compound combinations, concentrations, etc.) needed to meet increasing needs.

Approach: The NIST Traceable Reference Materials (NTRM) program has been created as part of the solution to this problem. An NTRM is a commercially produced reference material with a well-defined traceability linkage to existing NIST standards for chemical measurements. This traceability linkage is established via criteria and protocols defined by NIST and tailored to meet the needs of the metrological community to be served. Initially the NTRM concept was implemented in the gas standards area to allow NIST to respond to increasing demands for high quality reference

materials needed to implement the “Emissions Trading” provisions of the Clean Air Act of 1990 (while facing the reality of constant human and financial resources at NIST). The program has been highly successful and since its inception, ten specialty gas companies have worked with us to certify nearly 4200 NTRM cylinders of gas mixtures, which have been used to produce approximately 400,000 NIST-traceable gas standards for end-users.

The NTRM model for the commercial production of reference materials is being extended to other mature and high volume areas so that more of our resources can be diverted to address new and/or more difficult high priority measurement problems. For the benefit and protection of both the users and providers of these materials, NIST is in the process of trade marking the term NIST Traceable Reference Material (NTRM) in order to restrict its use to only those materials that meet NIST-defined criteria and specifications. Brief descriptions of each of the four areas where NTRM programs are in place or are being developed follow.

Gas NTRM Program (*F. Guenther and W. Dorko*)

The Gas NTRM program was defined to achieve maximum customer confidence in NTRM gas mixture products from Specialty Gas Companies (SGCs). At the time the program was defined it was thought that direct NIST involvement in the certification of the NTRM batches was desirable and necessary. Through this approach we have gained acceptance of these standards by the EPA, the automobile industry, and the stationary source measurement community. We now feel that the program can evolve to lessen the direct involvement of NIST in every NTRM batch. Over the next year we will be defining an alternative certification approach, which will allow SGCs who have demonstrated success through the production of NTRMs over a three-year period. This new approach will certify a particular SGC facility such that any gas cylinder analyzed on a NIST certified analytical system has the potential of being named an NTRM. Adequate controls will be imposed by NIST to assure quality control and traceability to NIST, however the SGC would be able to produce as many NTRMs as they require. It is hoped that this approach will enhance the availability of gas NTRMs such that they will replace gas SRMs as the primary traceability vehicle to U.S. Customers.

Another eventual outcome of this new approach would be the worldwide acceptance of gas NTRMs.

Optical Filters NTRM Program (*G.W. Kramer and J.C. Travis*)

NIST has produced Standard Reference Materials for calibrating the wavelength scale and verifying the absorbance accuracy of UV/visible chemical spectrophotometers for several decades. The NIST production capacity is rapidly becoming insufficient to meet the demand, and a recently developed program to leverage NIST measurement capability through the private sector is being adapted to these standards. NIST-Traceable Reference Materials (NTRMs) are produced and marketed commercially, but with the active participation of NIST in the testing and value assignment of the standards. The first NTRMs for chemical spectrophotometry will be on the market within the coming year, and will be modeled on NIST SRM 930e and NIST SRM 1930, neutral density glasses (in a cuvette-simulation format) certified at five wavelengths in the visible spectral region and spanning absorbances between 0.3 and 2.0.

The expanded uncertainties for the certified values will be kept close to those of the corresponding NIST standards by reducing the recertification period from two years to one, which will be compatible with the renewal cycle of many quality control protocols and will provide more frequent cleaning of the filters. The certifying laboratories will be accredited through the NIST-based National Voluntary Laboratory Accreditation Program (NVLAP) and will maintain periodic intercomparison measurements with the National Reference Spectrophotometer in the Analytical Chemistry Division of NIST. Other spectrophotometric NTRMs for wavelength calibration and UV absorbance verification are expected to follow.

Elemental Solutions NTRM Program (*G. Turk and M. Salit*)

A workshop was held at NIST on June 3, 1999 for major commercial producers of elemental solution standards. The components of a proposed NTRM program were presented to attendees. The key elements of this program include:

-The introduction of a new series of SRMs. Elemental Primary Standards, or EPS SRMs.

-A calibration transfer method that will compare the NTRM against the EPS SRMs. These measurements would be performed or contracted by the NTRM provider

-Proficiency testing. The ability of the NTRM provider to distinguish between slightly different amounts of analyte in different EPS containers has been proposed, and could be combined with the calibration function by keeping the EPS values unknown to the NTRM providers.

-Software to perform the value assignment of the NTRM with the appropriate uncertainty based on the data of the calibration transfer method. The software (which might be Web-based) will “unlock” the assigned value only if the proficiency test is passed.

-Periodic assessment of NTRM lots by NIST.

We have begun to implement important aspects of this proposal within the framework of the existing SRM Single Element Standard Solutions certification program. We have designated a few NIST Primary (NP) materials, and are preparing and using weighed aliquots of NP solutions (prototype EPS) for value assignment of the Spectrometric Solutions using specially designed high precision ICPOES methods.

Metal Alloy NTRM Development (*J. Fassett and R. Greenberg*)

The first steps in producing metal alloy NTRMs were outlined at a meeting held July 22 and 23, 1999, with the company Analytical Reference Materials International, a secondary metal alloy standards producer which has agreed to work with NIST to pioneer the NTRM concept for metals. A protocol document was prepared and discussed, and the trial process begun, with the intention to “fine tune” the protocol as the process proceeds forward. The company has submitted a proposal to produce 3 NTRM candidate materials:

- AISI Low Alloy Steel
- Chrome-Moly Steel F-11
- AISI 1030 Carbon Steel.

The benchmarks to be used to provide NIST traceability will be from the existing NIST 1700 Series of Low Alloy Steels. Analytical methods to underpin the accuracy of metals SRM and NTRM certification have been developed within the Division in support of the metals NTRM and SRM programs. A quaternary alloy (designated MP35N) has been extensively analyzed within the Division in this development/demonstration exercise. The following techniques have reported results at NIST:

- *Wavelength Dispersive XRF:* Complete elemental analysis, including 19 elements;

- *Glow Discharge OES:* Comparative measurements to the 16 elements determined by industry, including important non-metals (C, P, S, Si, and B);
- *Cold Neutron Prompt Gamma Activation Analysis:* B and C;
- *Instrumental Neutron Activation Analysis:* Majors Constituents (Co, Cr, Mo, Ni) and Mn;
- *ID-TIMS:* S;
- *High precision ICP-OES:* Major Constituents (Co, Cr, Mo, Ni); and
- *Radiochemical Neutron Activation Analysis:* (P).

We need to stress that these capabilities are for the most part new to the Division. Both XRF and GD-OES measurements were made on instruments acquired in the last year with the hope that they could support the metals program, in addition to other programs in the Division. The high precision ICP-OES work was a demonstration experiment that supports our contention that this instrumental technique has primary measurement character—high precision and controlled potential sources of systematic error—and is a candidate replacement for traditional, labor-intensive classical methods. The application of ID-TIMS (for S) and the nuclear methods represent unique capabilities at NIST and are not routinely used by industry. These techniques provide an accuracy benchmark that is also unique, underpinning method-dependent (and standards-dependent) techniques used by industry.

17. Accreditation of the First Class of Commercial Proficiency Testing Study Providers for EPA/States Water Programs

R.M. Parris, W.E. May, R.C. Christensen, E.A. Mackey, J.R. Moody, B.J. Porter, S.D. Rasberry, T.W. Vetter and C.D. Faison (NIST National Voluntary Laboratory Accreditation Program)

Objective: To establish a system under which private sector companies and interested states are accredited by NIST to provide proficiency testing (PT) that meets the needs of EPA and states to those laboratories testing drinking water and wastewater for regulated chemical, microbial, and radiochemical parameters.

Problem: Since the 1970's, EPA has conducted semiannual proficiency testing to assess the competence of over 6,000 public and private sector laboratories to conduct analyses required by the Clean Water and the Safe Drinking Water Acts. In 1998, the cost-free provision of these services was phased out to be replaced by a multiprovider system in which interested states and private companies provide these PT services on a fee-basis. Mechanisms and tools to provide appropriate government oversight of these programs were needed.

Approach: In a government-private sector partnership, NIST worked with the EPA, States, and other public and commercial entities to establish appropriate oversight of this new effort to externalize and improve the nation's environmental laboratory PT programs. Under this arrangement.

EPA:

- provided NIST with support to develop a program for private sector/state provision of PT studies, and
- works with States and NIST to assure that the program developed for (1) preparing, value-assigning and distributing PT samples and (2) evaluating the quality of the Environmental Testing Laboratory data is sufficient to support national/state water program needs.

NIST:

- developed and manages program for third-party accreditation of private sector water PT study providers,

- establishes and maintains SRMs to support the program, and
- conducts blind sample audits of the commercially supplied PT samples on an ongoing basis as part of our QA responsibility for the program.

PT Study Providers:

- develop, manufacture, value-assign, and distribute PT samples,
- score results of Environmental Testing Laboratory analyses,
- report results to participants, EPA, NIST, States, and appropriate accrediting authorities, and
- maintain accreditation through NIST National Voluntary Laboratory Accreditation Program (NVLAP).

Results and Future Plans: Following extensive discussions among the various stakeholders as to the roles/requirements of the program, a NIST handbook describing the technical requirements of this accreditation program was drafted, presented for comments, and published: NIST Handbook 150-19, Chemical Calibration: Providers of Proficiency Testing. NIST NVLAP accredits laboratories for their competence to characterize samples and to conduct proficiency test programs to support USEPA requirements for environmental laboratories; technical oversight of the program and the evaluation process is provided by the NIST/ACD. In November 1998, NIST NVLAP began accepting applications for accreditation in this new field, Providers of Proficiency Testing, for the provision of chemistry and microbiology PT studies as described in EPA's "National Standards for Water Proficiency Testing Studies: Criteria Document" (US EPA, December, 1998 Version). NVLAP program designations for providers of radiochemistry PT studies will be added after US EPA has delineated the EPA requirements for these studies in its criteria document.

In October 1999, the first class of nine accredited providers in the Chemical Calibration: Providers of Proficiency Testing program were announced by NIST/NVLAP. Applicant providers still undergoing evaluation will be added to the list on a case-by-case basis as accreditation is granted. A listing of the accredited providers and the specific program codes for which they are accredited are listed in a published directory and on an on-line directory at the NVLAP website, <http://ts.nist.gov/nvlap>. The

current June 1999 version of NIST Handbook 150-19 can also be obtained at this site.

NIST is producing primary benchmark materials such as SRMs for those parameters not covered by existing SRMs to provide the infrastructure needed by NIST to audit the commercially supplied PT samples and to assist providers in value-assigning their PT materials.

18. Strategic International Collaborations and Comparison Activities

W.E. May, J.D. Fassett, G.W. Kramer, M.M. Schantz, M.J. Welch, F.R. Guenther, K.W. Pratt, and R.M. Parris

Objective: To assess and document international comparability for chemical measurements among the world's national chemical metrology laboratories and to link such comparability to the U.S. and North American systems of chemical measurement traceability for improved accuracy in chemical measurements.

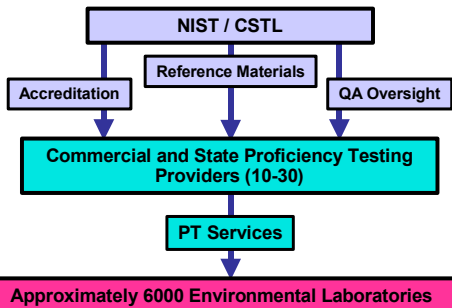
Problem: The need for demonstrating comparability and traceability of chemical analysis data is becoming recognized worldwide. Chemical measurements play a key role in the diagnosis and treatment of diseases, identification of global trends in the state of the biosphere, and the evaluation of the effects of various contaminants in the environment are only possible on the basis of reliable data. A significant proportion of industrial production and international trade is also dependent on chemical measurements. The uncertainty in the validity and/or lack of recognition of many of these measurements leads to a considerable amount of repeated measurements, particularly by regulatory agencies on imported products. This is expensive and impedes the free flow of international trade.

Leveraging ACD Resources

NIST/EPA Proficiency Testing Program



CSL, NVLAP, EPA, state and local governments, and private sector laboratories working together to establish a proficiency testing system for waste water and drinking water testing



- Issued NIST 150-19: Chemical Calibration - Providers of Proficiency Testing
- Received 12 applications for *Testing Providers*
- Producing primary benchmark materials where SRMs are not available
 - to provide infrastructure and primary standards needed to audit commercial *PT samples*
 - to assist providers in value assigning their *PT materials*

Approach: In October of 1999, nations and economies signed a "Mutual Recognition Arrangement between National Metrology Institutes for recognition of National Measurement Standards and of Calibrations, and Measurement Certificates. The Analytical Chemistry Division is a key participant in efforts of the International Committee for Weights and Measures (CIPM) and its Consultative Committee on Amount of Substance (CCQM) to address the issues of comparability and traceability for chemical measurements. The CCQM has begun to assess chemical measurement comparability through strategically selected intercomparisons among national chemical metrology laboratories in the general areas of advanced materials, biotechnology, commodities, the environment, food, forensics, health, pharmaceuticals, and general analytical applications. The Division has participated in all 15 of the intercomparisons that have been undertaken to date. The Division is also using the assessment exercises conducted through the CCQM for selecting partners for strategic bi- or trilateral collaborations to determine and document the comparability of NIST primary methods and standards with those of other nations and/or metrological regions. The Division holds the Chair for the Chemical Metrology Working Group within the Interamerican System of Metrology (SIM) and past chair for the NORAMET subregion.

Results and Future Plans: The CCQM has formed five working groups: (1) gas analysis, (2) organic analysis, and (3) inorganic analysis, (3) pH and Conductivity, and (4) Key Comparisons. These working groups are responsible for selecting and overseeing the operation of key comparisons that address chemical measurement-related issues important for international trade, environmental, health, and safety-related decision making. The Division is very active and has led various activities within all five working groups.

The Division provides the official leadership for the chemical metrology activities within SIM. Because the capabilities of the 34 countries within SIM span such a broad range, activities have initially been focused on training and capability assessment. Since only 3 of the 34 countries have formal programs in chemical metrology, we conducted the following courses during the past year for current or

designated future leaders of chemical metrology programs within SIM:

Organic Analytical Metrology; December, 1998; 12 participants
Spectrochemical Metrology; December, 1998; 14 participants
Nuclear Analytical Metrology; April, 1999; 6 participants
Classical Methods; May, 1999; 13 participants
Gas Metrology; June, 1999; 10 participants

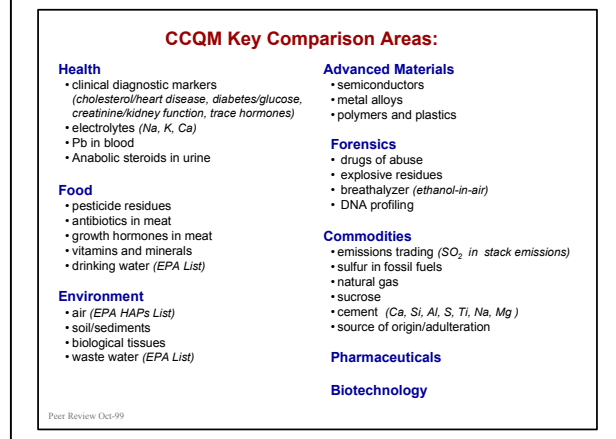
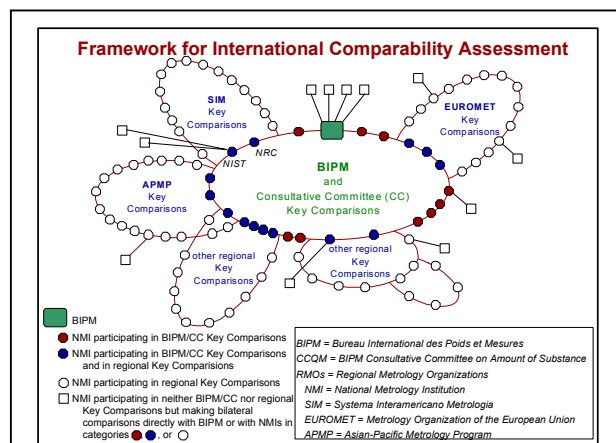
We also identified six intercomparison exercises to test the proficiency of NMI's or their designated collaborators for addressing chemical measurement problems within the Americas.

- *SIM-QM-P1*: Chlorinated Pesticides in Organic Solvent.
- *SIM-QM-P2*: Trace Metals in Drinking Water
- *SIM-QM-P3*: Automotive Exhaust Emission Gases
- *SIM-QM-P4*: pH (5-7 range)
- *SIM-QM-P5*: Vitamins and Minerals in Infant Formula
- *SIM-6*: Holmium oxide

The NORAMET subregion of SIM consists of NIST, NRC-Canada, and CENAM-Mexico. All three institutes produce Certified Reference Materials (CRMs) and have agreed to extract intercomparison data while assisting in each other's reference materials certification campaigns. The following intercomparisons took place during the past year using this paradigm:

- Metals in Drinking Water [CENAM]
- Elements in Sediments and Mussel Tissue [NRC]
- Organics in Sediments and Fish Tissue [NIST]
- Methyl Hg in Fish Tissue [NIST]
- Vitamins and Minerals in Milk Powder [CENAM]

For six years we have been involved in a strategic bilateral program with the National Measurement Institute (NMI) of The Netherlands for determining the equivalence of primary gas standards. Our activities have resulted in a formal "Declaration of Equivalence" that is mutually recognized by the U.S. EPA and European environmental regulatory bodies as documenting the equivalence of eight NIST and NMI primary gas mixtures suites (spanning a wide range of concentrations). In previous years the carbon dioxide, carbon monoxide, ethanol, oxygen, propane, nitric oxide, and sulfur dioxide PSMs have been shown to be equivalent. During the past year we have worked to establish equivalence in natural gas standards and have continued efforts to address a bias of 2% observed between NIST and NMI primary standards for hydrogen sulfide. Additional collaborations for assessing the equivalence of primary standards have been established with DFM (Denmark) and OHM (Hungary) for conductivity, with the PTB for pH, with EMPA (Switzerland) for elemental solution standards, with NIMC for volatile organic compound standards, with INPL (Israel) for moisture in oils, and with NPL (UK) for optical absorbance filter standards.



DECLARATION OF EQUIVALENCE
The National Institute of Standards and Technology - NIST
Gaithersburg, MD, United States of America
and
The Netherlands Measurements Institute - NMI
Delft, The Netherlands

NIST and NMI declare that on July 1, 1999 the suites of primary standard gas mixtures developed and maintained in both the Institutes, comprising a range of analyte concentrations in the stated diluent gas as listed in Annex 1, can be considered as equivalent within the stated uncertainties. This declaration shall expire on July 1, 2001 at which time a new declaration shall take effect.

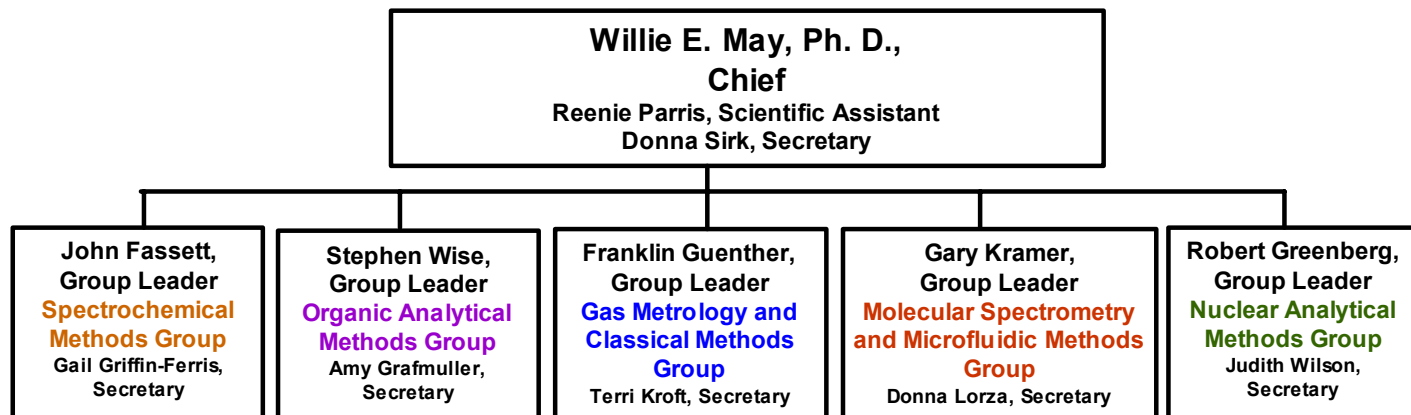
This declaration is based on the results of intercomparisons carried out between the two Institutes. A continuous program of intercomparisons has been agreed to in order to maintain this declaration and is outlined in a mutual Memorandum of Understanding, effective July 1, 1999.

Declaration of Equivalence

Annex 1: NIST and NMI Primary Standard Gas Mixture Suites which are declared to be equivalent

Component	Molar Fractions (mole/m ³)	Maximum Allowable Difference	Date of Reassessment
Carbon Dioxide	10x10 ⁻⁶ to 20x10 ⁻²	0.3 % relative	2000
Carbon Monoxide	10x10 ⁻⁶ to 10x10 ⁻²	0.3 % relative	2001
Ethanol	75x10 ⁻⁶ to 500x10 ⁻⁶	1 % relative	2002
Oxygen	0.1x10 ⁻² to 25x10 ⁻²	0.3 % relative	2003
Propane	10x10 ⁻⁶ to 1x10 ⁻²	0.3 % relative	2002
Nitric Oxide	10x10 ⁻⁶ to 1x10 ⁻²	0.5 % relative	1999
Sulfur Dioxide	100x10 ⁻⁶ to 1x10 ⁻²	0.5 % relative	2002
Natural Gas	Typical	1 % relative (CH ₄ 0.3 %)	2000

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